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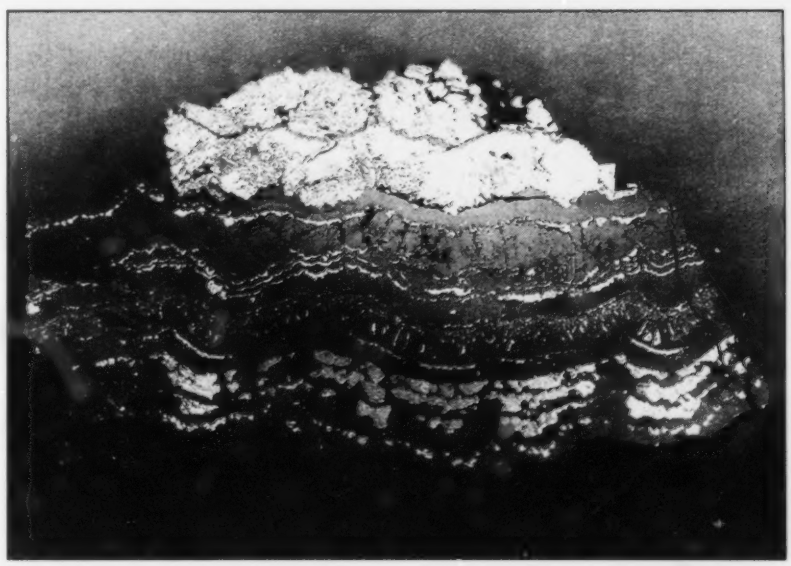
Indium Deposits and their Economic Potential:

Report on a Mission to Japan

G.J.A. Kooiman and A.A. Ruitenberg



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New Nouveau Brunswick

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Cover:
A sample of banded indium-bearing zinc-lead ore from the Toyoha Mine, southwest Hokkaido, Japan.

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INDIUM DEPOSITS AND THEIR ECONOMIC POTENTIAL: REPORT ON A MISSION TO JAPAN

SUMMARY

This report contains information that was collected during a recent mission (March 14-27, 1992) to Japan. The geology, mining, and economic potential of indium deposits are discussed. The information collected is relevant to the potential development of the tin–base-metal sulphide deposits of Mount Pleasant, New Brunswick, in which indium constitutes a prominent component.

The report is based on visits to mines, concentrators, and a specialty metals plant. In addition, discussions were held with key personnel of the Geological Survey of Japan, the Metal Mining Agency of Japan, Mitsui Mining and Smelting Co. Ltd., and the Canadian Embassy.

CONCLUSIONS

Indium-bearing tin–base-metal (ITB) deposits are among the most important known sources of indium in the world: The Toyoha Mine in southwestern Hokkaido is the largest known ITB deposit in Japan. The Mount Pleasant ITB deposit in southwestern New Brunswick is one of the largest known ITB deposits outside of Japan and contains twenty-five per cent of the world's indium reserves.

ITB deposits in Japan were emplaced in a transpressive (dextral shear) tectonic regime: This transpressive shear zone was activated about 9 Ma. The Mount Pleasant Deposit was emplaced in a similar tectonic environment during Late Devonian time.

ITB deposits of economic importance were generated by highly specialized, siliceous, fluorine-rich intrusions: A recent hypothesis suggests that the Toyoha and other deposits in southwestern Hokkaido were formed as a result of andesitic volcanism. This hypothesis appears to be based upon incorrect interpretation of radiometric age data.

Microscopic examination and microprobe analysis of polished thin sections show that ITB ores are mineralogically very complex: These deposits contain an abundance of elements including Cu, Pb, Zn, Sn, In, W, Au, Ag, Co, Bi, Se, Te, Ga, V, and others. Exsolution textures involving numerous sulphide minerals are characteristic.

The Kuroko Deposits in Japan are not significant sources of indium: The Kuroko Deposits locally contain between < 1 ppm to 18 ppm In, but no economically significant deposits occur in this geologic environment. In contrast to ITB deposits, the Kuroko Deposits formed in a rifting-type tectonic environment.

Domestic indium production in Japan has peaked: The Japanese mining industry is in decline as a result of high mining costs, dwindling ore reserves, and environmental constraints. Domestic indium production is derived almost exclusively from a single source, the Toyoha Mine. This mine has limited reserves and is also a high-cost underground producer. Additional reserves could become available if techniques can be developed to operate in areas with rock temperatures of up to 200°C, but this would further increase production costs.

Japan is becoming increasingly dependent on foreign indium supplies: More than 50 per cent of the domestic market depends on indium imports to meet increased demand. It is expected that the dependency on foreign supplies will continue to increase. France and China are presently their main suppliers, whereas North American producers are minor suppliers.

High-demand projections for indium: There is a rapidly growing demand for indium coatings. Most applications include indium-tin-oxide coatings in liquid crystal displays. Examples range from digital watches and portable computers to high-definition colour television. The market for portable computers is expected to increase five-fold

in the coming years.

High level of research and development: Japanese companies are continuing to invest heavily in research and product development to remain competitive and profitable. They are world leaders in indium applications and will remain so in the foreseeable future. In Japan, Korea is seen as the main future competitor in Southeast Asia.

Japan's main interest is in base metals: Most of Japan's overseas metallic mineral deposit investments are located in developing countries to secure base-metal supplies for their manufacturing industry, at least for the next two decades. The presently successful Japanese economy bases its future plans on the proposition that value lies less in owning sources of raw materials than in manufacturing secondary products. For example, copper concentrates are imported from all major copper-producing countries, Canada being the largest supplier. Value is added in Japan by manufacturing 99.9999% pure copper for stress-free audio cables.

RECOMMENDATIONS

1. Involve selected Japanese companies such as: **a.** Nippon Kinzoku (formerly Nippon Mining Company Ltd.). This company is the largest manufacturer of indium products in Japan. It operates a fully integrated indium industry. **b.** Dowa Mining Co. Ltd. with its extensive extractive metallurgy experience would be a prime candidate for research on the extraction of indium from concentrates. **c.** Mitsui Mining and Smelting Co. Ltd. has a commitment to invest in the Province of New Brunswick. Mitsui operates downstream indium production facilities, but does not own indium-bearing ores. **d.** Sumitomo Metal Mining Co. is a leader in the development of indium application technology.

2. Create trust and rapport through repeated meetings: Doing business with the Japanese requires time and an atmosphere of trust. Consensus has to be carefully cultivated. Therefore, several meetings are necessary to generate this rapport and commitment. Annually, a business conference that includes mining is held between Japanese and Canadian executives. It would be desirable for the Province of New Brunswick to be represented at these conferences. This year the conference was held in Yokohama in May.

3. Continue collaboration with the Geological Survey of Japan: Several years of direct contact with a research geologist of the Geological Survey of Japan proved to be very beneficial to the success of this mission. Japanese geologists have been studying indium ores for a long time and a transfer of information is essential. In addition, the involvement of the Geological Survey of Japan in further research at Mount Pleasant will create interest and trust among Japanese companies.

4. Effective presentation: The presentation of facts and figures, full-colour brochures, or even videos should receive high priority. This is very important because very few Japanese are fluent in English. Moreover, the Japanese have a highly developed artistic sense that they use diligently to convey information about their products. In other words, the wrapping is as important as the contents of the package. This concept also applies to scientific information.

5. Focus on downstream indium production opportunities: Indium contained in zinc concentrates has little or no value. Indium should be concentrated at the site to a saleable product such as indium sponge grading ten per cent In or more. The manufacture of indium metal or end products would be preferred.

The production of indium provides an excellent opportunity for the mining industry of New Brunswick to make the transition from a raw material producer to a very high value-added end product manufacturer. This will create wealth and a sustainable metals industry. Involvement of the Japanese indium industry is essential in order to achieve these goals.

SOMMAIRE

Ce rapport résume une visite au Japon (du 14 au 27 mars 1992) et contient une discussion de la géologie, de l'exploitation minière et du potentiel économique des gisements d'indium. L'information amassée au cours de cette visite est pertinente en ce qui a trait au développement possible du gîte de métaux de base et d'étain de Mount Pleasant, au Nouveau-Brunswick, dans lequel l'indium est un composant important.

Ce rapport repose sur des visites de mines, de concentrateurs de métaux et d'installations spécialisées en métaux de base ou en métaux plus rares. En outre, des pourparlers ont été entamés avec le personnel de la Commission géologique du Japon, la *Metal Mining Agency* du Japon, *Mitsui Mining and Smelting Co. Ltd.* ainsi que l'Ambassade canadienne au Japon.

CONCLUSIONS

Des dépôts de métaux de base et d'étain à teneur d'indium (MEI) sont parmi des sources d'indium les plus importantes au monde: La mine Toyoha, dans le sud-ouest de l'île d'Hokkaido, est le plus grand dépôt de MEI au Japon. Le gisement de Mount Pleasant, au sud-ouest du Nouveau-Brunswick, est un des plus grand gisements de MEI en-dehors du Japon et contient vingt-cinq pour cent des réserves mondiales d'indium.

Les gisements de MEI du Japon furent mis en place sous un régime tectonique transpressif (à cisaillement dextre): Cette zone transgressive était active il y a 9 millions d'années. Le gisement de Mount Pleasant fut mis en place sous un régime tectonique similaire, au Dévonien supérieur.

Les dépôts de MEI d'importance économique sont associés à des intrusions siliceuses riches en fluor: Une hypothèse récente suggère que le dépôt de Toyoha, ainsi que d'autres gisements du sud-ouest de l'île d'Hokkaido, résultent du volcanisme andésitique. Toutefois, cette hypothèse semble être basée sur une interprétation erronnée des âges radiométriques.

L'examen microscopique et l'analyse à la microsonde électronique de lames minces polies montrent que les minerais de MEI sont minéralogiquement très complexes: Ces dépôts contiennent une abondance d'éléments chimiques: Cu, Pb, Zn, Sn, In, W, Au, Ag, Co, Bi, Se, Te, Ga, V et autres. Des textures d'exsolution entre divers minéraux du groupe des sulfures sont caractéristiques.

Les gîtes de type Kuroko du Japon ne sont pas des sources importantes d'indium: Les gîtes de type Kuroko contiennent entre < 1 ppm et 18 ppm d'indium, mais aucun dépôt d'importance n'a été découvert dans cet environnement géologique. Les gîtes de type Kuroko se forment sous un régime de rift et contrastent ainsi avec les gîtes de MEI.

La production domestique d'indium au Japon a atteint un sommet: L'industrie minière japonaise est présentement en déclin à cause du coût élevé de l'exploitation minière, de l'épuisement du minerai et des contraintes environnementales. La production domestique d'indium provient presque exclusivement de la mine de Toyoha dont les réserves sont limitées, et la production souterraine coûte cher. Des réserves additionnelles seraient disponibles à condition de développer de nouvelles techniques d'exploitation minière dans des roches dont la température s'élève jusqu'à 200°C. Toutefois, cela ne ferait qu'augmenter les coûts de production.

Le Japon devient de plus en plus dépendant de l'approvisionnement étranger: Plus de cinquante pour cent du marché domestique dépend des importations d'indium pour satisfaire une demande accrue. Les principaux fournisseurs sont présentement la France et la Chine alors que l'Amérique du Nord contribue des quantités mineures.

Projections pour une demande élevée en indium: Un taux de croissance élevé est anticipé pour l'utilisation d'enduits d'indium. Les enduits d'oxyde d'indium et d'étain dans les écrans à cristaux liquides constituent l'application la plus courante. L'indium est utilisé, entre autres, dans les montres digitales, les ordinateurs portatifs et les téléviseurs couleur de haute résolution. On s'attend à ce que le marché des ordinateurs portatifs se multiplie par

cinq au cours des prochaines années.

Niveau élevé de recherche et développement: Les compagnies japonaises continuent à investir dans des programmes de recherche et de développement afin de rester compétitives et lucratives. Les Japonais sont les chefs de file quant aux applications de l'indium et ils le resteront dans un avenir prévisible. Au Japon, la Corée est pressentie comme le principal futur concurrent dans le sud-ouest Asiatique.

Le Japon s'intéresse en particulier aux métaux de base: Afin de sécuriser l'approvisionnement de leur industrie manufacturière pendant les vingt prochaines années, les Japonais ont investi surtout dans les pays en voie de développement. Le succès actuel de l'économie japonaise est fondé sur des plans d'avenir avec la prémice que la valeur est moins dans l'appropriation des matières premières que dans la fabrication des produits secondaires. Par exemple, une valeur est ajoutée aux concentrés de cuivre au Japon, les concentrés provenant de tous les principaux pays producteurs, avec le Canada comme fournisseur principal, en fabriquant du cuivre pur à 99.9999% pour des câbles audio *stress-free*.

RECOMMANDATIONS

1. Choisir et impliquer des compagnies japonaises telles que: **a.** Nippon Kinzoku (antérieurement Nippon Mining Company Ltd.). Cette compagnie est le plus grand manufacturier de produits d'indium du Japon. Cette compagnie opère une industrie d'indium entièrement intégrée. **b.** Dowa Mining Company Ltd. a une expérience en métallurgie extractive et serait un candidat de choix pour la recherche en extraction d'indium à partir de concentrés. **c.** Mitsui Mining and Smelting Company Ltd. s'est engagé à investir au Nouveau-Brunswick. Mitsui opère des usines de production des dérivés d'indium, mais n'est pas propriétaire de minerais d'indium. **d.** Sumitomo Metal Mining Company est un chef de file dans le développement des applications de l'indium.

2. Créer un climat de confiance et d'harmonie à partir de rencontres régulières: Faire des affaires avec les Japonais demande du temps et une atmosphère de confiance. Un consensus doit être attentivement cultivé. Par conséquent, plusieurs rencontres sont nécessaires avant de générer harmonie et engagement. Une conférence d'affaires, abordant le sujet de l'exploitation minière, est tenue annuellement entre les dirigeants de compagnies canadiennes et japonaises. Il serait approprié que la Province du Nouveau-Brunswick soit représentée à ces conférences. Cette année, la conférence a eu lieu en mai à Yokohama.

3. Continuer la collaboration avec la Commission géologique du Japon: Plusieurs années de contact direct avec un géologue de recherche de la Commission géologique du Japon s'avèrerait bénéfique pour le succès de cette visite. Les géologues japonais étudient les minerais d'indium depuis longtemps et un transfert d'information est essentiel. De plus, l'implication de la Commission géologique du Japon dans des recherches futures à Mount Pleasant créera à la fois un intérêt et un climat de confiance parmi les compagnies japonaises.

4. Présentation efficace: La présentation des faits et des chiffres, des brochures en couleur, ou même des vidéos devrait avoir une haute priorité. Ceci est très important car peu de Japonais parlent l'anglais couramment. En outre, les Japonais ont un sens artistique développé qu'ils utilisent à bon escient pour présenter de l'information sur leurs produits. En d'autres mots, l'emballage est aussi important que le contenu et cela s'applique tout aussi bien pour l'information scientifique.

5. Se concentrer sur les productions qui demandent de l'indium: L'indium contenu dans les concentrés de zinc n'a aucune valeur. L'indium devrait être concentré sur place en un produit vendable tel que les "éponges" d'indium qui contiennent 10 pour cent d'indium ou plus. La production d'indium métallique ou d'autres produits finis serait préférée.

La production d'indium procure une excellente opportunité pour l'industrie minière du Nouveau-Brunswick de faire la transition entre un producteur de matière première et un manufacturier qui ajoute une plus-value à un produit fini. Ceci créera une richesse et un soutient à l'industrie métallique. La participation de l'industrie japonaise de l'indium est essentielle pour atteindre ces buts.

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INDIUM INDUSTRY OF JAPAN

Japan is the largest producer, importer, and consumer of indium in the world. Japan is also leading in the development of indium applications. The use of indium in thin film coatings for such applications as liquid crystal displays are expected to be the major area of market expansion. Liquid crystal displays are considered a product of increasing strategic importance, especially in the field of portable computers. The lap-top computer market is expected to increase five-fold in the next few years. Demand for indium in other applications has levelled off in recent years.

PRODUCTION FROM DOMESTIC SOURCES AND IMPORTS

According to officials at the Metal Mining Agency of Japan in Tokyo, four companies are involved in indium production: 1) Nippon Mining Co. Ltd.; 2) Dowa Mining Co. Ltd.; 3) Mitsui Mining and Smelting Co. Ltd.; and 4) Sumitomo Metal Mining Co. Ltd.

Nippon is the most important indium producer. The company is also fully integrated. The Toyoha Mine near Sapporo operated by Nippon, accounts for 90% of the total domestic production. Indium metal is produced at the Saganoseki plant near Oita on the southern island of Kyushu, whereas the production of indium alloys and high-purity indium takes place at Nippon's Isohara plant at Kitaibaraki City, northeast of Tokyo.

Dowa Mining Co. Ltd. operates the Kosaka metallurgical complex in northern Honshu. Indium is produced at Kosaka from Kuroko ores and possibly also from imported zinc concentrates.

Officials at the head office of Mitsui Mining and Smelting in Tokyo indicated that the company's zinc concentrates do not contain indium. Mitsui operates the Kamioka zinc smelter in western Honshu, which treats concentrates from the Kamioka zinc-lead skarn deposit and from Mitsui's Huansala Mine in Peru. One of Mitsui's divisions manufactures indium products. Mitsui expects an annual growth in this market of approximately ten per cent. No information is available about Sumitomo's involvement in the indium industry.

Statistics for production from domestic sources, imports, total production of indium products, and consumption are tabulated below in metric tonnes (Table 1). Japanese imports of indium products for 1990, specified by company and country, are given in Table 2.

TABLE 1. STATISTICS FOR PRODUCTION AND CONSUMPTION.	1984	1985	1986	1987	1988	1989	1990	1991 (est.)
Domestic Production	15	16	18	20	24	30	32	
Imports	1	8	21.5	31.0	29.6	31.5	36	
TOTAL PRODUCTION	16	24	39.5	51.0	53.6	61.5	68	
CONSUMPTION	18.4	22	40.2	47.8	51.8	57.7	63	65.9

TABLE 2. JAPANESE INDIUM IMPORTS DURING 1990.		
COMPANY	COUNTRY	METRIC TONNES
Metaleurop Companies	France/Italy	19.0
Various Companies	China	10.5
Metallurgie Hoboken/Overpelt	Belgium	2.8
Indium Corporation of America	U.S.A.	1.9
Cominco	Canada	1.2
Others		0.6
	TOTAL	36.0

PRODUCTION AND END-USE CONSUMPTION

The most important and fastest growing segment of the market is indium tin oxides (ITOs) that are used as thin film coatings on glass. The electrically conductive coatings are primarily used in liquid crystal displays (LCD's) for television screens, video monitors, and especially portable computer screens*. This indium end-use has been growing at 20-25% per year over the past three years, as illustrated in Table 3.

TABLE 3. GROWTH IN USE OF INDIUM TIN OXIDE (ITO) FROM 1988 to 1991.

YEAR	1988	1989	1990	1991
ITO end-use (metric tonnes)	15	17	20	25

ISOHARA METALS PLANT

Nippon Mining Co. Ltd. operates the Isohara specialty metals plant in the industrial park of the small coastal town of Kitaibaraki City, Ibaraki Prefecture. It is located about 150 km northeast of Tokyo.

The Isohara plant produces a great variety of metals and alloys including high-purity platinum, titanium, zinc, cadmium, and copper. Alloys include molybdenum and tungsten silicides, platinum-rhodium alloy wire, and cobalt-nickel. Indium products account for 40% of the Isohara output.

The plant employs 250 people, including 65 to 70 university graduates with degrees mostly in chemistry and metallurgy. The labour force has been recruited locally from Kitaibaraki City. About 60 employees are working in product development. Staff turnover is low. During the last two years, thirty-six new employees were hired and only one person left the employment of the company during that period. The plant was constructed six to seven years ago and an extension to the plant was completed last year. The site covers 265 000 m^2.

INDIUM SOURCE

Raw material for the Isohara plant is obtained from Nippon's Saganoseki metallurgical complex near Oita on the southern island of Kyushu. Indium from Saganoseki is shipped to Isohara in 500 g ingots, grading 99.99% In. Ingot size will be increased in the near future to 1000 g to improve handling.

Saganoseki is mainly a copper smelter and refinery that produces 300 000 tonnes of metal by using a flash smelting process and 180 000 tonnes by electro-refining. The plant also includes a lead smelter that produces 36 000 tonnes of metal. In addition, Saganoseki produces 920 000 tonnes of sulphuric acid and other products including indium.

INDIUM PRODUCTS

The indium ingots of Saganoseki are used at Isohara as follows:

	1000	kg/m for indium-tin alloys
	300	kg/m for pure indium solder
	100	kg/m for high-purity indium metal
	100	kg/m for indium phosphide and other products
Total	1500	kg/m or 18 tpy

The most important indium products at Isohara are indium-tin alloys used either as sputtering targets or tablets (Table 4).

At the time of our visit, the most common products were green, middle density ITO products (density 5.0 g/cm^3) consisting of a layer of ITO (the target) bonded on a copper backing plate by In solder. Backing plates with remnants of targets are returned by customers to the plant for rebuilding. Some customers prefer super high density quality ITO targets (density 6.7 g/cm^3).

High-purity indium metal (6N, 7N) is produced in the form of wire, shot, and small ingots. InP is produced as small wafers.

Recycling of indium will not affect the indium producers because of the high purities involved.

OUTLOOK FOR INDIUM

Management at the Isohara plant is very optimistic about the outlook for indium. Growth in demand for ITO products exceeded 20% during the last two years. The 1990 annual report of Nippon Mining Co. Ltd. stated "Especially noteworthy was the increase in the sales of the indium-tin-oxide targets for advanced display devices".

* The Japanese industry currently uses 38% of all indium in the form of ITO.

TABLE 4. INDIUM-TIN ALLOYS				
Product	Size (mm)	Purity %	Wt %	Density (g/cm^3)
ITM targets (Indium tin metal)	127*w* x 381*l* x *t* 203.2 (Dia) x *t*	In+Sn > 99.99	In:90 Sn:10	7.3
ITO targets (Indium tin oxide)	127*w* x 381*l* x *t* 203.2 (Dia) x *t*	In_2O_3 > 99.99 SnO_2 > 99.99	In_2O_3:95 SnO_2:5 or In_2O_3:90 SnO_2:10	4.0 - 6.4
ITO tablets (Indium tin oxide)	30 (Dia) x 7*t* 39 x 39 x 15*t* 45 x 45 x 20*t*	In_2O_3 > 99.99 SnO_2 > 99.99	In_2O_3:95 SnO_2:5	4.0 - 4.5

The Isohara plant currently uses 18 tpy of indium metal which constitutes about 70% of the Saganoseki plant output of 25 tpy (our estimate).

In the near future, the Isohara plant will take all of the Saganoseki output and additional indium metal may have to be imported from Europe and China.

ENVIRONMENTAL CONCERNS

The main environmental concerns in the Isohara plant are not so much the raw material or the products fabricated but the fluids used to clean equipment and tools.

COMPANY REORGANIZATION

During our stay in Japan, plans were announced to amalgamate Nippon Mining Co. Ltd. with the Kioseky Oil Company. The new company will be known as Nippon-Kioseky. A new metals company will be created under the name Nippon Kinzoku (Kinzoku-Metal).

THE KUROKO DEPOSITS

Information on the Kuroko Deposits in Japan was collected because these deposits are known to contain small amounts of indium. It was our objective to obtain more detailed information about the geology and mineralogy of these deposits and their possible significance as indium producers. Information on Kuroko-type deposits is also applicable to base-metal sulphide exploration in the Tobique and Annidale belts of New Brunswick, and other parts of Atlantic Canada.

After reviewing relevant literature on the Kuroko Deposits prior to our visit to Japan, we had general discussions about these deposits with Drs. Takeo Sato and Ryoichi Kouda of the Geological Survey of Japan in Tsukuba. Ryoichi Yamada, the Exploration Manager of Dowa Mining Co. Ltd., provided us with valuable detailed information about the Kuroko Deposits and guided an underground visit to the Fukazawa Mine.

TECTONIC SETTING AND CHARACTERISTICS

The type area of the Kuroko base-metal sulphide deposits is the Hokuroku Basin in northeastern Honshu, Japan (Sato 1974; Ohmoto 1983; Urabe and Marumo 1991) (Figures 1 and 2). The Hokuroku Basin and similar basins occur in the Green Tuff Region. This region comprises a volcanic belt more than 1500 km long that formed during an episode of Miocene rifting in the inner margin of the Japan Arc. This rifting episode was associated with the opening of the Sea of Japan that separated the island arc from the Eurasian continent between 21-14 Ma (Otofuji *et al.* 1985). Extensive bimodal basaltic-rhyolitic volcanism occurred throughout this period. The Kuroko Deposits mostly formed during the climax of the rifting episode between about 16 and 15 Ma (Nakajima 1988; Yamaji 1990).

The Kuroko Deposits are all intimately associated with submarine felsic volcanic rocks. The deposits are stratiform or stratabound lenticular bodies mainly composed of base-metal sulphides, silver, and gold. Abundant barium and calcium sulphates accompany the ores. Concentrates from the Kuroko Deposits also contain a few parts per million of indium (Murao *et al.*

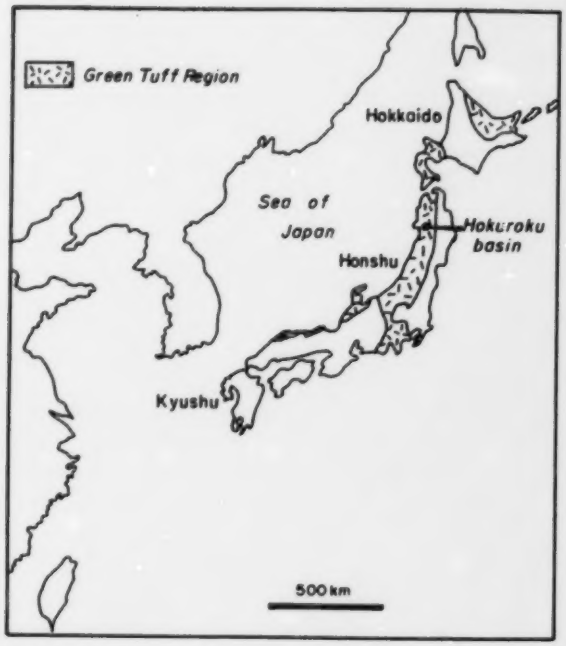


FIGURE 1. Location of the Green Tuff Region and Hokuroku Basin (after Urabe and Marumo 1991).

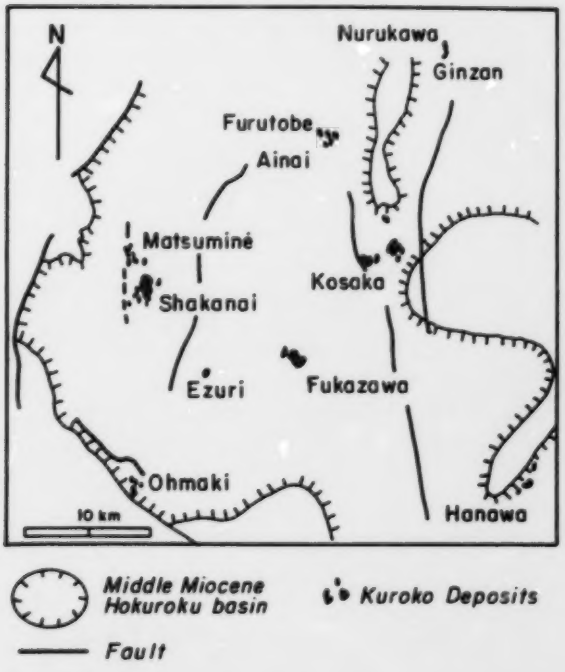


FIGURE 2. Location of the Kuroko Deposits in Hokuroku Basin (after Urabe and Marumo 1991).

1991).

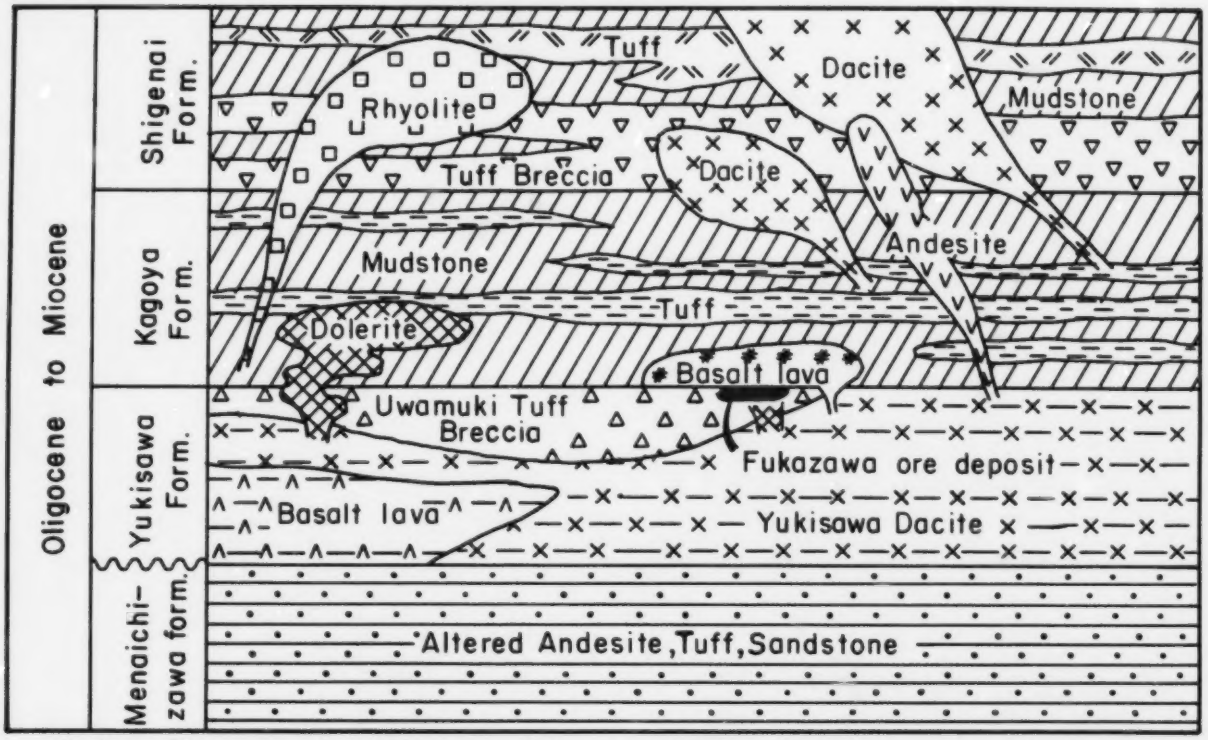
The Kuroko Deposits are commonly well zoned. In the stratiform deposits, the upper half of the deposits is rich in galena, sphalerite, and barite (black ore). Indium occurs in the black ores, but there are few published assays (Ryoichi Yamada, oral communication, 1992). The lower half of the deposits is dominated by pyrite and chalcopyrite (yellow ore). The stratiform orebodies are underlain by intensely silicified, disseminated, and stringer-type mostly copper-rich ores that occupy irregularly shaped, steeply plunging zones in felsic lavas and pyroclastics. Small lenses or thin beds of ferruginous chert commonly overlie the stratiform deposits (Sato 1974). Gypsum and/or anhydrite occur below or as lateral equivalents of the yellow ores (Ryoichi Yamada, oral communication, 1992). It is also notable that the deposits occur in several well-defined rock units (Nakajima 1988).

Although the Kuroko Deposits have numerous common characteristics, there are some significant differences (Ryoichi Yamada, oral communication, 1992). Some deposits, such as the large Matsumine Deposit (30 million tonnes) (Figure 2), are characterized by abundant yellow ore. The Kosaka Deposit is closely associated with a rhyolite dome and contains both abundant black and yellow ore (total 20 million tonnes). This deposit also contains extensive stringer and disseminated ore that occupies a mushroom-shaped body in a breccia zone overlying the rhyolite dome. The recently discovered Nurukawa Deposit is unusually rich in gold. The black ores in this deposit contain 10-20 g/t Au, the siliceous stringer and disseminated ores average 8-14 g/t Au and vein-type ores found below the stringer zone contain 100-1000 g/t Au (Ryoichi Yamada, oral communication, 1992).

FUKAZAWA MINE

The Fukazawa Deposit has become famous in the annals of mineral exploration because its discovery can be entirely attributed to precise interpretation of the regional stratigraphy and alteration patterns associated with the Kuroko Deposits. Exploration in this area was initiated after 1965 (Tanimura *et al.* 1974), when geologic mapping had demonstrated the presence of the upper horizon of the Yukisawa Formation or the Uwamuki Tuff Breccia. This horizon was known to host the Kosaka Mine (Figure 2). Between January 1969 and September 1970, 164 holes totalling 86 249 metres were drilled. Of these, 41 holes intersected ore.

TABLE 5. STRATIGRAPHY AT FUKAZAWA MINE
(after Tanimura *et al.* 1974).



Geology: The stratigraphy at the Fukazawa Mine (Tanimura *et al.* 1974) is shown in Table 5. The Yukisawa Dacite that occupies the footwall of the deposit was examined in detail in the mine. The unaltered dacite is a green, massive flow with small plagioclase phenocrysts. Near the orebodies, the dacite is greyish white to white due to intense sericitic and argillic alteration. The Yukisawa Dacite is overlain by the Uwamuki Tuff Breccia that hosts the ore deposit. This unit consists of intensely altered lithic tuffaceous rocks, breccia, and bedded tuffaceous rocks. The bedded tuff contains numerous flattened pumice fragments.

The ore section in the upper part of the Uwamuki Tuff Breccia is composed of three types of ore from bottom to top. These are: 1) typical stringer and disseminated ore; 2) low-grade yellow ore; and 3) massive black ore. The yellow ore and black ore are mostly conformable, but they are locally separated by massive barite. The black ore is overlain by massive basalt (Table 5). Most of the stringer and disseminated ore in the mine consists of pyrite, chalcopyrite, sphalerite, silver minerals, and gold. The yellow ore is composed of pyrite, chalcopyrite, bornite, enargite, and luzonite. The black ore consists of sphalerite, galena, tetrahedrite, tennantite, chalcopyrite, pearceite, stromeyerite, and polybasite.

In the exploration of the Fukazawa Deposit, rock alteration was used extensively in addition to stratigraphy (Ryoichi Yamada, oral communication, 1992). The two main alteration types that were used are: 1) the alteration of plagioclase to sericite and clay minerals that resulted in the replacement of sodium by potassium; and 2) alteration of magnetite to pyrite. In places where the regional stratigraphy was considered favourable, vertical holes were drilled at 1-km intervals. These holes were drilled to penetrate 75 m into the Yukisawa Dacite. Five samples were collected from each 75-m interval and were chemically analysed for sodium. The geometric mean of the five sodium assays was calculated for each hole. In areas where the sodium contents were < 0.4 % Na, holes were drilled at 250-m spacing and where ore was intersected the spacing was reduced to 100 m. The alteration of magnetite to pyrite was measured by determining the magnetic susceptibility of the footwall dacite. There was a problem with this method, however, because in intensely fractured zones, magnetite also alters to hematite. Pyrite and hematite cannot be distinguished by measuring magnetic susceptibility.

Mining Method: The Fukazawa Mine was the first trackless mine in Japan. The new Nurukawa Mine is also trackless.

Access to the Fukazawa mine is provided by a 2.2-km-long service ramp, grading 9° 45'. Ore is transported to surface via a conveyer ramp. The mining method that was developed in the sixties in the nearby Kosaka mine and adopted later in all Kuroko mines, is underhand cut-and-fill with an artificial roof. The remarkable aspect of this mining method is that nearly 100% of the ore is extracted from orebodies with a complex geometry.

Mining costs are high as is reflected in high cut-off grades of 8% combined Pb + Zn or 2.8% Cu. Black ore constitutes approximately 40% of the mill feed and siliceous stringer ore makes up the remaining 60%. The ratio in which the ores are blended depends on the grade of the black ore which commonly ranges from 25-40% combined Pb and Zn.

Mining takes place in the following sequence:

1. Development commences with the excavation of the main lower level, 20-30 m below ore level. Overhead core drilling is carried out at 20-m-spaced fans to delineate the orebody accurately. This is followed by establishing the upper level and inclined drift excavation. The upper and lower levels are connected by an ore pass raise. The lower level then becomes the haulage level. An air door is established on the lower level.

2. Stoping commences with horizontal gate drift stoping in the top of the orebody. Cross-cut stoping at right angles to the gate drift stoping starts when the ore has disappeared from the gate drift stope face. Ore excavation removes a 3-m-thick horizontal slice that is 5 m wide. All stopes have timber support. Blasting, mucking, and timbering cycles are coordinated to maintain a constant yield.

Four men are assigned to three stopes. The crew has one two-boom jumbo, one LHD (load-haul-dump) vehicle, and one Timbo (a timbering vehicle). The crew completes 1.5 cycles per shift in each stope. A two-way communication system is used to coordinate the utilization of equipment.

3. Filling commences with the levelling of the stope floor and steel bars are laid in a 2 m x 30 cm pattern. A floor containing 15% cement mortar is poured. This floor forms the roof of the next stope. A bulkhead is positioned where the roof is high and sound.

Discharge of the backfill takes place at the highest possible point. The backfill plant is located on surface. The hydraulic backfill is made up of volcanic ash and tailings, along with 3% cement mortar. The volcanic ash generates strong coagulation and quick dehydration. Only coarse tailing fractions are used. Separation of coarse fractions from fines takes place in the backfill plant by using cyclones. Once backfilling is completed in the top slice, gate drift stoping commences below the filled upper slice.

The mine employs 200 people, including 150 hourly paid employees and 50 staff. Miners are paid the equivalent of U.S. $17/hr., including two fixed bonuses.

MATSUMINE MILL

A description of the 1991 milling practices and a flow sheet of the Matsumine Mill are presented in Appendix A. An update is given below.

The Matsumine Mill is located about 8 km west of the Fukazawa Mine. At the time of our visit, the central processing plant of Matsumine near Odate was treating 36 000 tonnes/month Kuroko ores. Ore is trucked in from the Fukazawa Mine (18 000 t/m), Matsumine Mine (13 000 t/m), and the Nurukawa Mine (5000 t/m). The Ezuri Mine was mined out in September 1991.

The mill treats 2600 tonnes per day on a 14-day period and is then closed for a maintenance period of two weeks. The plant is highly automated and operated by only six people. These include two in crushing, two in flotation, one in filtration, and one in shipping. Operators in flotation rely heavily on data from the on-stream-analyser that monitors 12 streams.

The mill feed contains approximately 8% Zn, 2% Pb, 2% Cu, 10% pyrite, 10% barite, 1 g/t Au, 100 g/t Ag.

Concentrate grade and recovery at Matsumine Mill (1986 figures) are given in Table 6.

Copper concentrates are shipped to the Kosaka smelter, 15 km east of Odate. Au, Se, and Te are also recovered. Zinc concentrates are transported to the smelter near Akita (Akita Prefecture). Smelter residues containing Ga, Ge, and In are presumably shipped from Akita to Kosaka for further processing and metal recovery. Pb concentrates are shipped to the Hachinohe

smelter (Aomori Prefecture, northern Honshu). Pyrite concentrates are shipped to the Tobata smelter on the southern island of Kyushu. Bismuth is recovered from the retreatment of sinter of the pyrite concentrates. Bismuth and antimony are also recovered during lead refining.

INDIUM PRODUCTION FROM KUROKO ORES

The deposits of the Kuroko District are apparently not significant sources of indium. A few available assays of black ore from the Dowa-owned mines indicated a range from < 1 ppm to 18 ppm In. This confirms an observation made by Dr. Satoshi Murao that some of the Kuroko Deposits contain up to 20 ppm indium whereas others contain no indium. None of the Dowa officials met were certain about indium recovery, although the company videos indicated indium recovery at the Kosaka metallurgical complex. No indium production figures are available for the Kosaka plant.

INDIUM-BEARING TIN-BASE-METAL SULPHIDE DEPOSITS

The main geologic objective of the indium mission was to collect detailed information on the geologic setting, mineralogy, and economic potential of indium-bearing tin-base-metal sulphide vein deposits in Japan and, if possible, elsewhere in the world. It was expected that these data would be applicable to the Mount Pleasant indium-bearing tin-base-metal sulphide deposits.

During our visit we were provided with numerous well-illustrated papers on the mineralogy of various indium deposits in Japan and elsewhere (Murao and Furuno 1990, 1991*a*, *b*; Murao *et al.* 1991; Narui *et al.* 1988; Ohta 1989, 1991; Sawai *et al.* 1989; Seetharam 1986; Watanabe 1990*a*, 1991; Yajima and Ohta 1979; Yajima *et al.* 1991). In addition, we had detailed discussions about indium deposits with Drs. Satoshi Murao (G.S.J. Tsukuba) and Eijun Ohta (G.S.J. Sapporo). This included microscopic and electron probe examination of polished thin sections of typical indium-bearing tin-base-metal sulphide ores from various deposits in Japan and elsewhere. Photomicrographs were taken from ores that were not covered by previous publications. A copy of one of the most comprehensive published reports (Ohta 1991) is included in Appendix B.

TECTONIC SETTING AND CHARACTERISTICS

Unlike the Kuroko Deposits in northern Japan, the indium-bearing tin-base-metal sulphide veins were emplaced during the initial phase of a transpressive (dextral strike-slip) tectonic regime that was activated in the Japan Arc about 9 Ma (Nakajima 1988; Watanabe 1990*a*). This transpressive regime was generated by oblique subduction of the Pacific Plate beneath the Kuril Arc (North Japan) (Watanabe 1990*b*). During this period, the dominantly bimodal basaltic-rhyolitic volcanism (associated with the Kuroko Deposits) was replaced by mostly unimodal andesitic and sporadic rhyolitic volcanism (Watanabe 1990*a*).

The largest known indium deposit in Japan is the Toyoha tin-polymetallic vein system in southwest Hokkaido (Yajima and Ohta 1979). Other vein deposits in this district include the Chitose, Eniwa, Koryu, Kobetsuzawa, and Todoroki (Au, Ag); Teine (Au, Cu); Ohe and Inakuraishi (Mn-Pb-Zn) deposits (Watanabe 1990*a*) (Figure 3). These vein systems are hosted by hydrothermally altered Miocene strata. The Miocene strata are intruded by quartz porphyry, dated 8.5 Ma (Igarashi *et al.* 1978), and are unconformably overlain by unaltered Pliocene to Pleistocene andesite lavas. Therefore, the unaltered andesite lavas were considered to postdate mineralization (Yajima and Ohta 1979).

Yajima and Ohta (1979) emphasize that a number of polymetallic vein deposits in southwest Hokkaido show

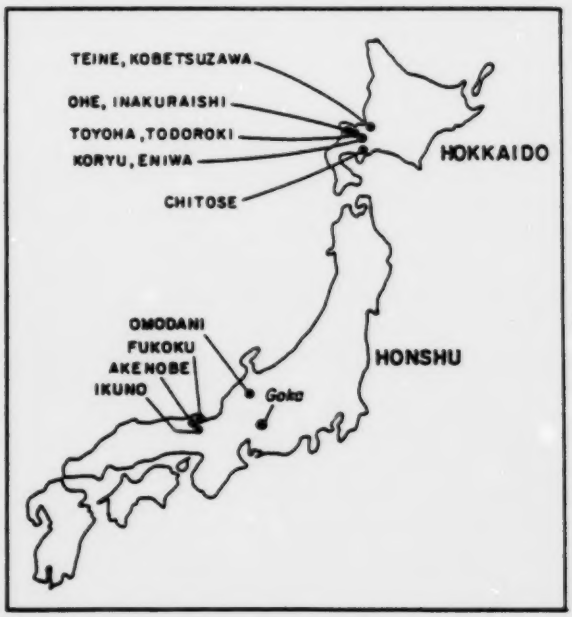


FIGURE 3. Location of the main indium-bearing and other vein deposits in Japan (after various publications of Mining Geology and Canadian Mineralogist).

TABLE 6. CONCENTRATE GRADE AND RECOVERY AT MATSUMINE MILL (1986)		
CONCENTRATE	GRADE (%)	RECOVERY (%)
Cu	23	93
Pb	56	66
Zn	55	93
Py	49	75
$BaSO_4$	97	50
Au		70
Ag		88

a clear zonal distribution around the quartz porphyry intrusions. This suggests a possible genetic relationship. However, K/Ar dating of micas associated with alteration haloes enveloping the polymetallic veins in southwest Hokkaido yielded ages ranging from Pliocene to Pleistocene. These mineral ages are similar to K/Ar whole-rock ages obtained from the andesite lavas (Watanabe 1990*a*). Consequently, he suggests the possibility that the indium-bearing polymetallic veins in southwest Hokkaido may be related to andesitic volcanism. It seems more likely, however, that the deposits predate the andesite flows and are associated with the quartz-porphyry intrusions as suggested by Yajima and Ohta (1979). Resetting of K/Ar ages of the micas in the alteration haloes enveloping the deposits could have occurred during subsequent andesitic volcanism.

In southwest Japan, there are several other indium-bearing tin–base-metal sulphide deposits that are associated with intensely fractionated granitic intrusions. These intrusions are very siliceous, are fluorine-rich, are mostly ilmenite-bearing, and have extremely high Rb/Sr ratios. The Goka, Akenobe, Ikuno, Fukoku, and Omodani deposits are the largest in this area (Murao and Furuno 1990, 1991*b*; Shimizu and Kato 1991).

In other parts of the world, indium-bearing polymetallic vein systems are also associated with granitic intrusions and include the Tosham Deposit in India, the Dachang and Gejiu deposits in China, several deposits in Central Peru (Murao *et al.* 1991), and the Mount Pleasant Deposit of New Brunswick in eastern Canada. The Mount Pleasant Deposit is one of the largest deposits known in the world and contains over 1000 tonnes of indium or about 25 % of the known world reserves. It is notable that this deposit is associated with a granitic complex that has similar chemical characteristics (Ruitenberg and Fyffe 1982; Sinclair *et al.* 1988; McLeod 1990) to those of the intrusions that generated the indium-bearing polymetallic veins in southwest Japan (Murao and Furuno 1990, 1991*a*, *b*).

A review of the literature and a microscopic examination of numerous polished thin sections of various indium-bearing ores demonstrated that all these ores are mineralogically very complex and contain an abundance of elements including Cu, Pb, Zn, Sn, In, W, Au, Ag, Co, Bi, Se, Te, Ga, V, and others (Yajima and Ohta 1979; Ohta 1989; Murao and Furuno 1990, 1991*a*, *b*; Murao *et al.* 1991; Yajima *et al.* 1991). Exsolution textures involving numerous sulphide minerals are most characteristic (Figures 4, 5, 6 and Appendix B). These textures reflect mixing of the hydrothermal fluids and ore emplacement over an extended period of time. It is notable that these textures are also well developed in the indium-bearing tin–base-metal sulphide ores at Mount Pleasant (Petruk 1973; Kissin and Owens 1989).

THE TOYOHA MINE

Geology: The Toyoha Mine comprises an epithermal polymetallic vein system hosted by Miocene volcanic and sedimentary rocks that are unconformably overlain by Pliocene and Quaternary strata (Table 7). Alteration associated with the deposits does not extend into the younger strata.

The Toyoha Deposit consists of more than 55 veins (Figure 7) that occur over an area 4000 m long and

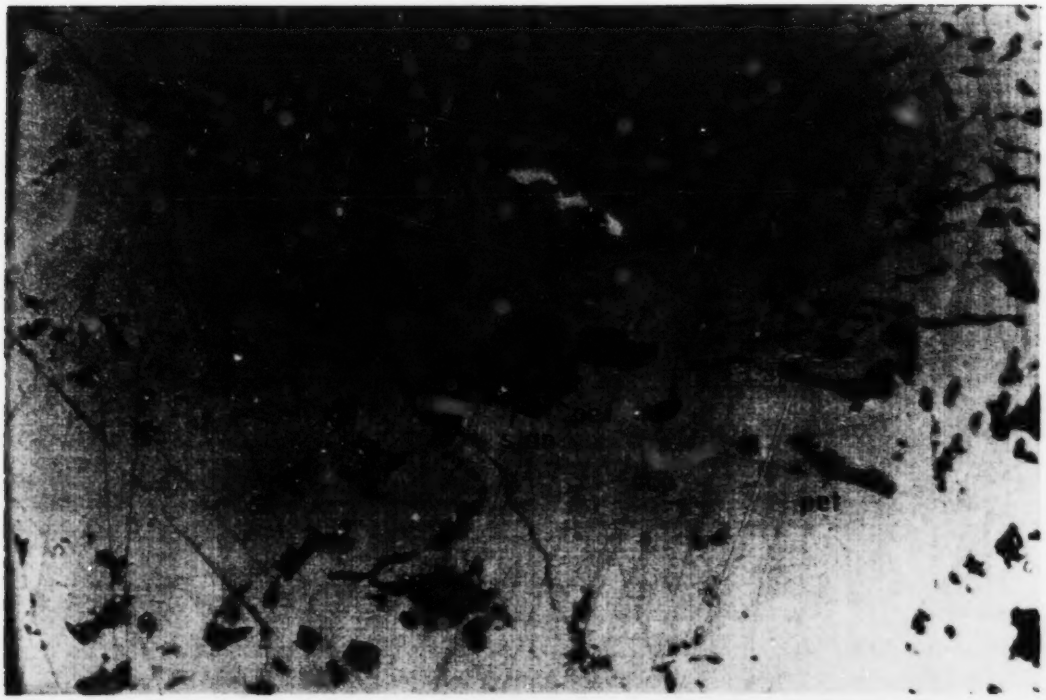


FIGURE 4. Photomicrograph (220X) showing petrukite (pet) exsolution rods in chalcopyrite (ccp). Petrukite locally contains indium-bearing stannite (stan) (light grey); Goka Mine, southwest Japan.

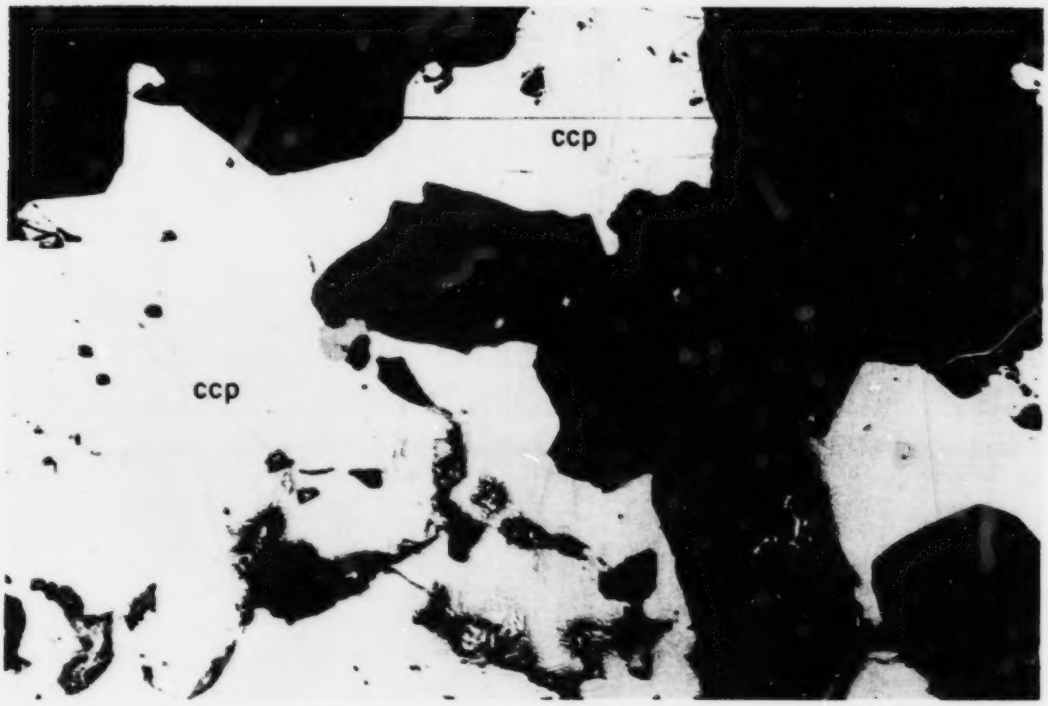


FIGURE 5. Photomicrograph (220X) showing chalcopyrite (ccp) with inclusions of sphalerite (sp) [containing small exsolution blebs of chalcopyrite] and roquesite (roq); Akenobe Mine, southwest Japan.

FIGURE 6. Photomicrograph (220X) showing chalcopyrite (ccp) in part replaced by indium-bearing stannite (stan); Tosham Deposit, India.

1500 m wide (Toyoha Mines Co. Ltd. 1990). The deposit is being mined to a depth of 450 m, but diamond drilling has demonstrated that the veins extend at least to 650 m.

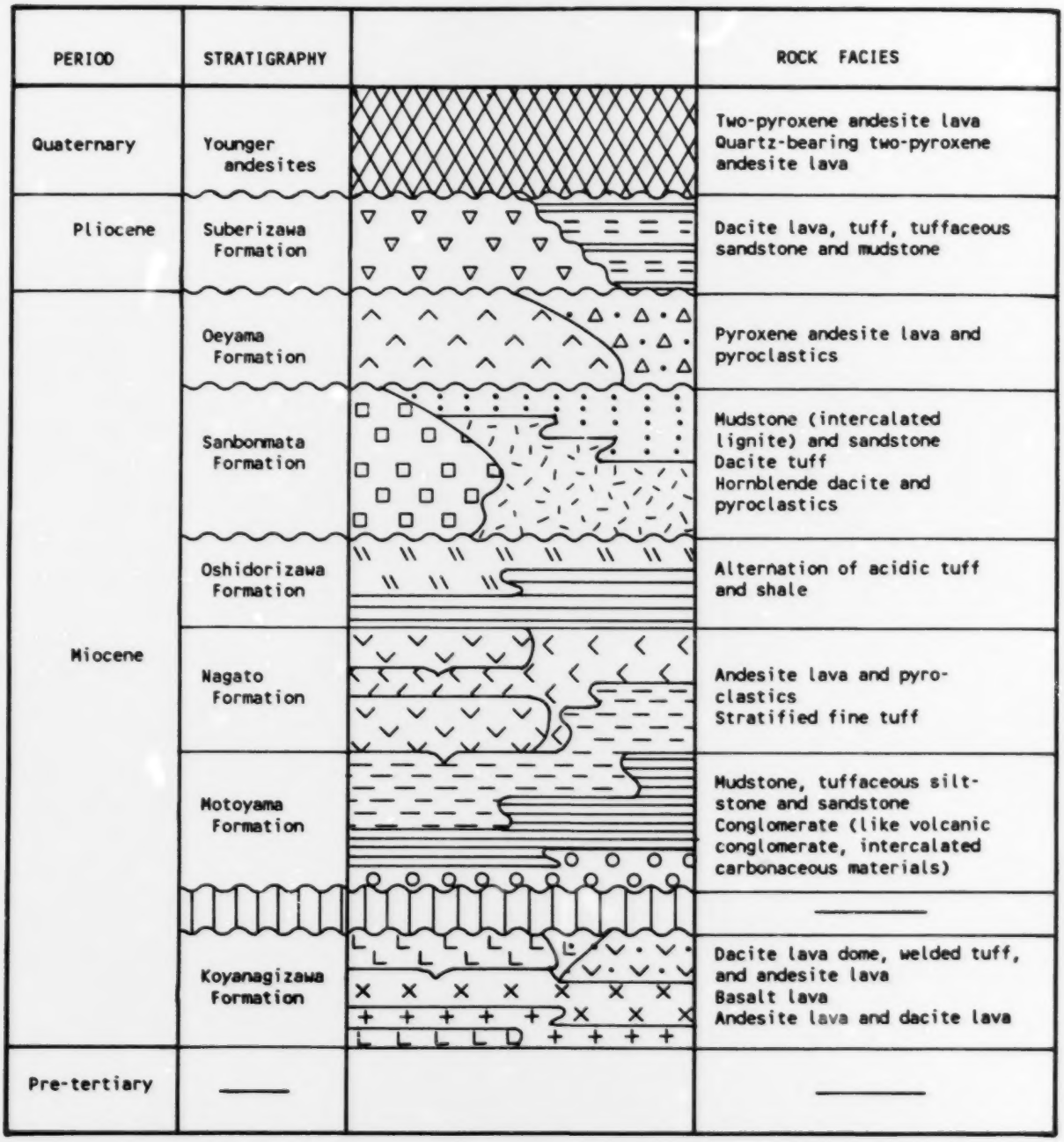
Cross-cutting relationships between various veins in the mine have demonstrated two major mineralization stages. The early one is divided into two sub-stages and the later one into five (Table 8) (Toyoha Mines Co. Ltd. 1991; Ohta 1989; Yajima and Ohta 1979). The early-stage mineralization, which formed the Tajima and Harima veins in the central part of the mine area, contains little or no indium. In contrast, the late-stage Sorachi, Izumo, and Shinano veins are relatively rich in indium. Underground examination and sampling of one of the late-stage veins revealed three types of ore that include massive sphalerite, banded sphalerite and galena, and mixed sphalerite-galena-chalcopyrite. The chalcopyrite in the footwall, at least in part, cuts across the sphalerite and galena. Indium is most abundant in the banded unit (oral communication, Eijun Ohta, 1992). Micaceous alteration and silicification are associated with all the vein systems.

Mining Methods: A 1990 summary of the mining practices at the Toyoha Mine is given in the Appendix C. An update is provided here.

The mining method used is sub-level stoping. Mining blocks are 30 x 50 m. The upper level and lower level (undercut) are spaced at 50-m levels with sub-levels in between. Raises are drilled to define the ore blocks. Blast holes are 55 or 105 mm in diameter and ammonium nitrate is used as an explosive. Production is 80 tonnes per man shift. Ore drawing is carried out with load haul dump (LHD) equipment. The ore is hauled from stope drawpoints to a central ore bin above the main haulage level. Ore haulage on this level is done by Granby cars to the main haulage shaft.

About twenty per cent of the mining costs are applied to heat control. Rock temperatures in current working places reach up to 120-160°C due to a very steep geothermal gradient. The vein system is open at depth and toward the southeast where rock temperatures reach 200°C. Heat-proof explosives currently in use are safe for a period of 24 hours at 160°C. Considerable research is being undertaken to develop safe explosives for use in 200°C conditions.

TABLE 7. STRATIGRAPHY AT TOYOHA MINE



Heat control is achieved by:

1. Forced Air Ventilation: This ventilation system provides a combined intake airflow of 26 000 m^3/min. The sinking of the No. 7 shaft near the Shinano vein greatly improved ventilation. As a result, air temperatures were reduced from 50-55°C to around 32-35°C.
2. Cold Water Spraying: Cold water spraying is carried out on working faces. This results in a temperature reduction of 10-15°C.
3. Removal of Geothermal Fluid: This removes large

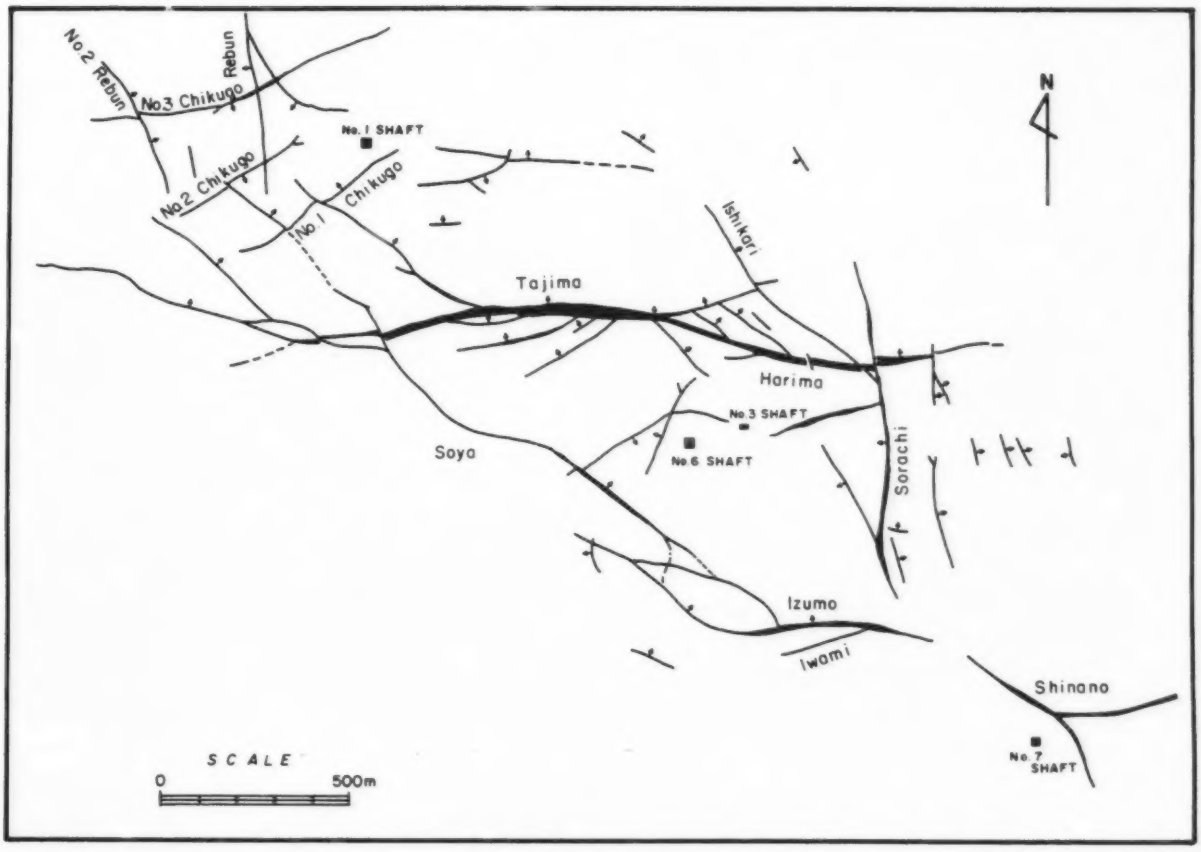


FIGURE 7. Vein system, Toyoha Mine, southwest Hokkaido, Japan (after Toyoha Mines Co. Ltd. 1990).

amounts of heat from the underground workings.

4. Air Conditioning of Equipment: This assists in making working conditions more acceptable.

Milling: A 1991 outline of the Toyoha mill is attached in Appendix D. An update is provided here.

The concentrator treats 45 000 tonnes per month. Ore is supplied from the following veins:

	Izumo Vein	10 000 t/m
	Shinano Vein	15 000 t/m
	Sorachi Vein	5000 t/m
	Soya Vein	4000 t/m
#3	Chikugo Vein	3000 t/m
#2	Chikugo Vein	4000 t/m
	Development Rock	4000 t/m
		45 000 t/m

The flotation section operates with conventional flotation cells that produce lead, zinc, and recently, copper concentrates. In addition, 2.7-m-diameter column flotation cells are used to clean the concentrates. These cells were installed 3½ years ago to accommodate an increased pyrite content of the ore and resulting lower zinc concentrate grades.

Column cells were installed for the following reasons: 1) to improve the cleaning circuit; 2) to decrease power consumption; 3) to increase capacity; and 4) to reduce labour requirements through automation.

After the column cells were installed the following results were obtained: 1) capacity increased to 93 t/hr; 2) quality of the concentrates increased by 2%; 3) power requirements were reduced by 6%; 4) per tonne cost of reagents was reduced by 100 yen/t; and 5) repairs were decreased.

The column flotation cells were obtained from BHP-

TABLE 8. CHARACTERISTICS OF MINERALIZATION STAGES AT TOYOHA MINE

STAGE	MAIN ORE MINERALS	GANGUE MINERALS	ACCESSORY MINERALS	SILVER MINERALS	AU CONTENT ELECTRUM	COMPOSITION TETRAHEDRITE	FeS IN SPHALERITE	Pb/Zn RATIO	MINOR ELEMENTS	VEIN STRUCTURE
STAGE I	Galena Sphalerite Pyrite	Quartz	Hematite Magnetite Mn-silicates	Argentite Native Silver Electrum	0-30 mol%		3 mol%	0.5		Massive
STAGE II	Pyrite	Calcite Quartz Rhodochrosite Mn-silicates								Banded
STAGE IIIa	Pyrite	Quartz	Cassiterite Wolframite Arsenopyrite Pyrrhotite Marcasite Tetrahedrite Stannite	Tetrahedrite Ag-Bi-minerals (rich in silver)	30-50 mol%	Sb/(As+Sb) <0.5 at% Ag content av. 3 wt%			W Sn Co	
STAGE IIIb	Pyrite Chalco-pyrite								Bi In	
STAGE IV	Galena Sphalerite Pyrite		Arsenopyrite Pyrrhotite Marcasite Stannite	Ag-Sb-sulfosalts Tetrahedrite (poor in silver)		Sb/(As+Sb) 0.7 – 08 at% Ag content av. 15 wt%	7-8 mol%	0.1	Sn W In	Massive Brecciated
STAGE V	Galena Sphalerite Wurtzite Pyrite	Sericite Kaolinite Dickite	Arsenopyrite Pyrrhotite Marcasite Stannite	Ag-Sb-sulfosalts Tetrahedrite Ag-Sn-minerals Ag-In-minerals (rich in silver)		Sb/(As+Sb) 0.9 at%< Ag content av. 21 wt%	6-7 mol%	0.4	Sn W In	Banded
STAGE VI	Galena Sphalerite Pyrite	Quartz Chlorite	Pyrrhotite Marcasite				5-6 mol%	0.3		Crustifi-cation, Brecciated
STAGE VI	Pyrite	Calcite, Quartz Rhodochrosite Mn-silicates								

Utah's Island Copper operation on Vancouver Island, British Columbia in western Canada.

INDIUM RECOVERY

The average grade of Toyoha ore is 0.014% In (1991 figures). At a monthly production rate of 45 000 tonnes, the contained indium amounts to 6.30 tonnes. Toyoha produces 7400 tonnes of zinc concentrates assaying 0.084% In. The contained indium in zinc concentrates is 6.22 tonnes. The recovery of indium in zinc concentrates according to this calculation is almost 99%. It is more likely that the indium recovery equals the zinc recovery of approximately 96%. The losses of indium to lead, copper, and pyrite concentrates and to tailings appear to be minor.

The indium-rich zinc concentrates are transported by road (50 km summer road, 100 km winter road via Sapporo) to the port of Otaru and shipped to the Mikkaichi smelter of Nikko Zinc Co. Ltd., located in the Toyama Prefecture on central Honshu. Indium recovery at the Mikkaichi smelter is only about 30% in the form of flue dust. The flue dust is shipped to Nippon's Saganoseki plant for the production of indium metal. The Toyoha mine does not receive payments for the indium in zinc concentrates.

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APPENDIX A. MILLING PRACTICES AT THE MATSUMINE MILL

APPENDIX A

MILLING PRACTICE AT MATSUMINE MINE 1991

The Matsumine mill treats 37,000 tons' crude ore per month. The mining production of the Matsumine mine, the Fukasawa mine and the Ezuri mine at present are 12,000 tons, 16,000 tons and 4,000 tons each per month. Another 5,000 tons' ore come from the Nurukawa mine that belongs to New Uchinotai Mining Co.

The crude ore is classified to two types. One is "Black ore", that contains chalcopyrite, bornite, tetrahedrite, tennantite, galena, sphalerite, pyrite, barite etc., and the other is "Yellow ore", that contains much quantity of pyrite and chalcopyrite.

The flowsheet is shown in Fig. 1.

CRUSHING

The ore, crushed to -100mm in underground, is transported and stored in the stockyard.

In the crushing plant, the ore is crushed to -25mm by Gyratory crusher and Cone crusher, after washing and desliming by Drum scrubber.

The crushed ore is conveyed to 8 fine ore bins and stored separately depending on the kind of ore.

The fine particles in the slime are recovered by screw decanter and fed to the grinding circuit.

GRINDING

The ore is ground in three stages by Rod mill and Ball mills.

The proportions of -200 mesh size of the ground ore are 70%.

FLOTATION

1. Cu-Pb bulk flotation
   The pH value is regulated to 5.5 with sulfurous acid and lime to depress sphalerite and pyrite.
   Dithiophosphate is used as a collector.
2. Cu-Pb separation
   The pulp is heated to 60°C and activated carbon is used to depress galena.
3. Zn flotation
   The pH value is regulated to 8.5 in rougher and to 11.5 in cleaner with lime. Copper sulphate and ethylxanthate are used.
4. Pyrite flotation
   The pH value is regulated to 4 with sulfuric acid and ethylxanthate is used.
5. Barite flotation
   Aeropromoter #825 is used as a collector and sodium silicate as a depressant.

CONCENTRATES & TAILINGS

Each concentrate is filtrated and transported to smelters.

The coarse sand in the tailings is returned to the mines for filling, and the fines and slimes are pumped to the dam.

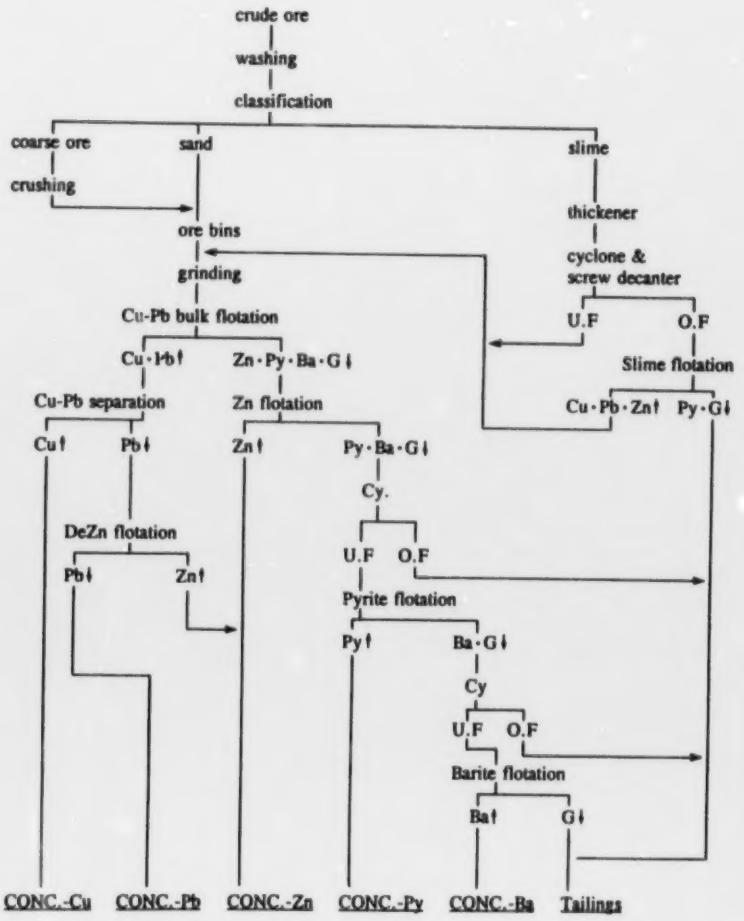

Fig. 1 Flowsheet

PRODUCTION

PRODUCT	Wt%	ASSAY (g/T, %)							DISTRIBUTION (%)						
		Au	Ag	Cu	Pb	Zn	PyS	$BaSO_4$	Au	Ag	Cu	Pb	Zn	PyS	$BaSO_4$
MATSUMINE	32.4	0.65	65.0	2.70	1.15	3.40	19.00	6.00	20.63	25.45	55.84	17.53	16.67	61.57	29.35
FUKASAWA	43.2	0.50	70.0	1.00	2.40	8.30	6.20	5.80	21.16	36.54	27.58	48.79	54.24	26.79	37.83
EZURI	10.8	1.50	175.0	1.28	3.25	9.18	5.15	14.50	15.87	22.84	8.82	16.52	15.00	5.56	23.64
NURUKAWA	13.6	3.20	93.0	0.90	2.70	6.90	4.50	4.50	42.34	15.17	7.76	17.06	14.09	6.08	9.18
F E E D	100.0	1.02	82.8	1.57	2.13	6.62	10.01	6.63	100.00	100.00	100.00	100.00	100.00	100.00	100.00
CONC.-Cu	5.5	3.74	386.2	21.50	4.93	4.90	11.43	0.19	20.00	25.50	75.00	12.67	4.05	6.25	0.16
CONC.-Pb	2.6	12.01	990.3	5.22	55.00	5.29	2.16	2.03	30.00	30.50	8.50	66.00	2.04	0.55	0.78
CONC.-Zn	10.9	1.77	233.8	1.38	2.63	55.00	3.99	1.25	19.00	30.90	9.67	13.52	91.00	4.36	2.06
CONC.-Py	14.7	1.53	44.1	0.44	0.38	0.45	49.00	0.91	22.00	7.82	4.17	2.66	1.00	72.00	2.01
CONC.-Ba	3.4	0.16	5.5	0.04	0.13	0.12	0.55	96.50	0.54	0.23	0.08	0.21	0.06	0.19	50.00
TAILINGS	62.9	0.14	6.7	0.06	0.17	0.19	2.65	4.74	8.46	5.05	2.58	4.94	1.85	16.65	44.99
RECOVERY									69.00	86.90	83.50	66.00	91.00	72.00	50.00

Installed Power	9,100 KW
Power Consumption	35 KWH/T
Water Consumption	4.5 m^3/T
Operators	15
Maintenance	5
Staff	9
Total	29

CONDITIONS & CONSUMPTIONS

	pH	PD %	Temp. (°C)	-200mesh %	Consumption (g/T)												
					Nikko-125	AF-208	KL-234	Ethyl Xanthate	AP-825	Activated Carbon	Copper Sulphate	Sodium Hydrogen-sulfite	Sodium Dichro-mate	Sulfuric Acid	Sodium Silicate	Sulfurous Acid Gas	Lime	Fuel Oil
Cu-Pb Flota.	4.5~5.5	40		70	10	60	15									2500	1200	
Cu Flota.	5.0	30	65		1		5			10								2500
DeCu Flota.	6.0	20	50									10						
DeZn Flota.	7.5	15	65		1			2			20		40					
Zn Flota.	8.5~11.5	30			17			100			380						2300	
Py Flota.	4.0	40			1			400						1300				
Ba Flota.	6.0	40							90						60			
Slime Flota.	9.0~11.0	10		96	10		20											

APPENDIX B. POLYMETALLIC MINERALIZATION AT THE TOYOHA MINE, Hokkaido, JAPAN[1]

Mining Geology, 39(6), 355–372, 1989

Occurrence and Chemistry of Indium-containing Minerals from the Toyoha Mine, Hokkaido, Japan

Eijun Ohta*

Abstract: Toyoha lead-zinc-silver vein-type deposit in Hokkaido, Japan produces an important amount of indium as well as tin and copper. Bismuth, tungsten, antimony, arsenic, and cobalt are minor but common metals. Indium minerals recognized are; unnamed Zn–In mineral (hereafter abbreviated as **ZI**) whose composition is at the midst of sphalerite and roquesite, unnamed Ag–In mineral (**AI**) of $AgInS_2$ composition, roquesite (**RQ**) and sakuraiite. Observed maximum weight percentages of indium in chalcopyrite, kesterite (**KS**) and stannite are 1.0, 1.86 and 20.0, respectively. Indium concentration in sphalerite ranges from 0.0n to a few weight percent in most case, but exceeds ten weight percent at some points. Detailed EPMA analyses have revealed that such high concentration is attributed to a continuous solid solution between sphalerite (**SP**) and ZI. Continuous solid solutions between $RQ_{90}ZI_{10}$ and $RQ_{57}ZI_{43}$, and between $KS_{100}ZI_0$ and $KS_{30}ZI_{70}$ are also detected. These solid solutions are attributed to coupled substitutions of 2(Zn, Fe) for CuIn, and of (Zn, Fe)In for CuSn. Other substitutions found between chalcopyrite and stannite and between stannite/kesterite and roquesite are of $(Fe^{+2}, Zn)Sn$ for $2Fe^{+3}$ and of $(Fe^{+2}, Zn)Sn$ for 2In respectively. Economically most important indium carriers in Toyoha are ZI and indium-bearing sphalerite. Next to sphalerite are kesterite, stannite and the anisotropic chalcopyrite. The occurrence of these minerals indicates that these minerals have been formed by pulsatile mineralization whose peak temperatures were 50 to 100°C higher than the hitherto estimated maximum formation temperature, about 300°C, of the deposit.

Introduction

The Toyoha mine is located 40 km southwest of Sapporo, Hokkaido, Japan. The lead-zinc-silver veins are Pliocene to Pleistocene in age as indicated by potassium-argon dating (Sawai and Itaya, 1989), and are probably related to a series of latent intrusions (NEDO, 1988) which appear to be the heat source of current extensive geothermal activity around the mining area. Two formation stages of the veins have been discriminated (Akome and Haraguchi, 1963, 1967; Miyajima et al., 1971; Hashimoto et al., 1977). Veins of both stages produce subordinate amount of manganese in the northwest of the vein swarm, while a high-grade copper (more than one weight percent Cu) zone is recognized in the Shinano and Izumo veins on the southeast of the swarm (Kanbara et al., 1989). In addition, the later-stage veins in the southeast produce antimony, arsenic, tin, indium, bismuth, tungsten, cobalt and molybdenum (Yajima, 1977; Ohta, 1980; Ohta et al., 1987; Narui et al., 1988). The overall zonal distribution of these metals is concordant to that of silver minerals (Yajima and Ohta, 1979; Yoshie et al., 1986), of gangue minerals (Ohta and Marumo 1985), and of fluid inclusion data (Yajima and Ohta, 1979). This indicates that indium from Toyoha is related to the later-stage mineralization which centered on the southeastern border of the vein swarm. The average indium content in the crude ore from Toyoha is as high as 250 ppm (Yoshie et al., 1986), which is comparable to that in zinc concentrates (not in crude ore) of some representative indium producers in central Peru (Soler, 1987). It should be emphasized that the indium grade is far higher in the later-stage veins (Yoshie et al., 1986; Narui et al., 1988). This paper presents the occurrence and chemistry of indium-containing minerals from Toyoha to clarify the distribution and mode of occurrence of indium in ore minerals.

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Keywords: Toyoha vein-type deposit, Indium, Tin, Roquesite, Solid solution, Formation temperature.

Chemical features of newly identified solid solutions of the indium-containing minerals, and the formation temperature of the indium and tin minerals are discussed.

Table 1 Tin and indium minerals recognized in the Toyoha deposit.
CP-ST ss: chalcopyrite-stannite solid solution

name	ideal formula	reference
cassiterite	SnO_2	Yajima, 1977
hersenbergite	SnS	Ohta et al., 1987
berndtite	SnS_2	Ohta et al., 1987
teallite	$PbSnS_2$	Sugaki and Hayashi, 1986
canfieldite	Ag_8SnS_6	Ohta and Yajima, 1979
stannite	Cu_2FeSnS_4	Yajima, 1977
kesterite	Cu_2ZnSnS_4	this study
hocartite	Ag_2FeSnS_4	Kajima et al., 1979
pirquitasite	Ag_2ZnSnS_4	Kajima et al., 1979; Jonas and Picot, 1982
rhodostannite	$Cu_2FeSn_3S_8$	Sugaki and Hayashi, 1986
toyohaite*	$Ag_2FeSn_3S_8$	Ohta et al., 1987
Zn-In mineral	$CuZn_2InS_4$	Ohta, 1980
Ag-In mineral	$AgInS_2$	Ohta, 1980
roquesite	$CuInS_2$	this study
indium sphalerite	$(1-x)ZnS + 0.5xCuInS_2$	this study
sakuraiite	$(Cu,Fe,Zn)_3(In,Sn)S_4$	this study
CP-ST ss	$0.7Cu_2FeSnS_4 + 0.6CuFeS_2$?	this study

* New mineral (Yajima et al., in prep.)

Mineralization Stages of the Toyoha Deposit

Indium minerals commonly accompany tin minerals, and those from Toyoha are not exceptions. By this time seventeen tin and/or indium minerals have been recognized in the Toyoha deposit (Table 1). As already noted, these minerals are concentrated in the later-stage veins distributed in the southeast of the deposit, namely, Shinano, Izumo, Sorachi, and southern half of Soya (Fig. 1). The later-stage mineralization is subdivided into three (Ohta, 1980) or five (Kanbara et al., 1989) substages. Although the detail of subdivision is not confirmed yet, the sequence of the late-stage mineralization is summarized as follows:

A Characteristic minerals formed in this substage are pyrrhotite and iron-rich sphalerite. This corresponds to the substage III-a in Kanbara et al. (1989), and to the substage I in Ohta (1980).

B This substage is characterized by tin and

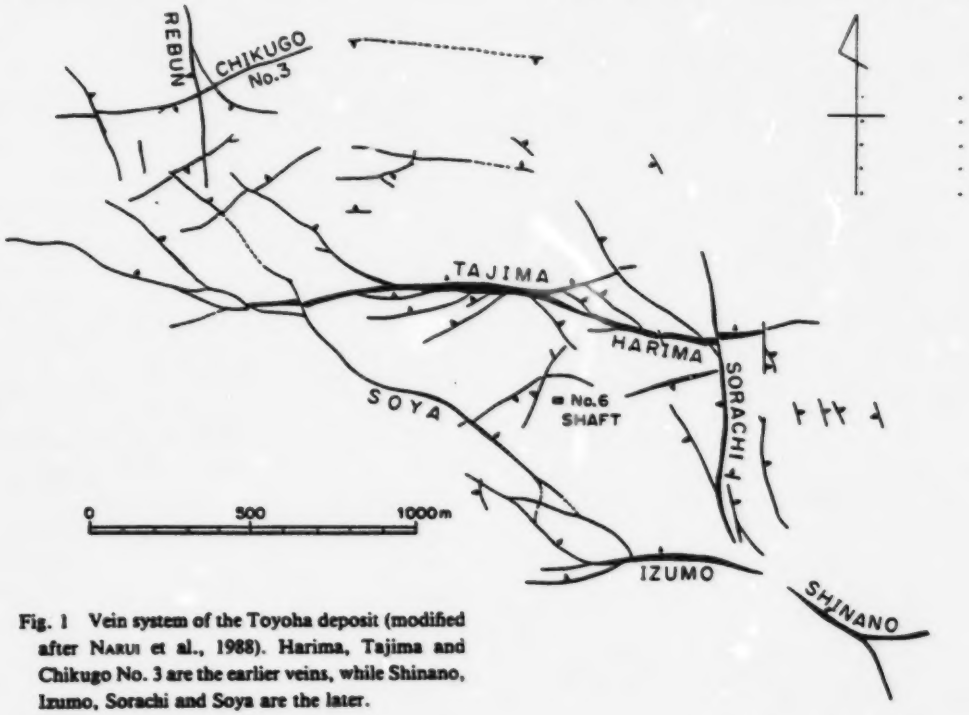

Fig. 1 Vein system of the Toyoha deposit (modified after Narui et al., 1988). Harima, Tajima and Chikugo No. 3 are the earlier veins, while Shinano, Izumo, Sorachi and Soya are the later.

indium minerals associated with chalcopyrite, sphalerite, galena, wolframite, and arsenopyrite. KANBARA's III-b and IV. OHTA's substage II.

C Substage of silver sulfosalts such as pyrargyrite, diaphorite and freibergite associated with galena and sphalerite. KANBARA's V. OHTA's substage III.

D Recognized only in northern half of the Soya vein. Sphalerite and galena in this substage are not associated with silver, tin nor indium minerals. KANBARA's VI.

E This is recognized mainly in the northwest of the deposit, and is characterized by manganese minerals. KANBARA's VII.

Occurrences and Microscopic Observations of Indium-Containing Minerals

Ag-In mineral (substage C):

The unnamed Ag-In mineral is rarely and locally recognized at middle to upper levels of the Sorachi vein where intense silver mineralization has followed that of tin and indium. It occurs in close association with hocartite, galena, pyrargyrite and pyrite as metasome which has partly replaced the Zn-In mineral or indium-bearing sphalerite (hereafter expressed as indium sphalerite). This suggests that the formation of the Ag-In mineral is due to a reaction between indium minerals of the substage B and the silver-rich ore solution of the substage C (OHTA, 1980). As compared with hocartite, the Ag-In mineral has similar polishing hardness, and shows a slightly more red tint. Its anisotropism is strong, but bireflectance is not observed.

Zn-In mineral and indium sphalerite (substage B):

The unnamed Zn-In mineral has a chemical composition at the midst of sphalerite and roquesite. It is common in the later-stage veins, and usually occurs within sphalerite (OHTA, 1980). It generally shows concentric parallel intergrowth with normal and indium sphalerite. Stannite, kesterite, and chalcopyrite often accompany them. A unit band of the Zn-In mineral is as wide as 50 microns at lower levels of the veins, but is quite thin, generally ten microns or less, at upper levels. Under ore microscope, the Zn-In mineral exhibits a slight brown tint as compared with sphalerite, and shows imperceptible to weak anisotropism, but no bireflectance nor internal reflection. Its polishing hardness is similar to that of sphalerite. Indium sphalerite is commonly observed as thin growth bands within normal sphalerite, and exhibits various colors between those of normal sphalerite and the Zn-In mineral. Though boundaries of the Zn-In mineral against the other two are generally sharp, indium sphalerite frequently shows gradational boundaries to normal sphalerite. Fig. 3-A shows a back-scattered electron image of rhythmically zoned indium sphalerite.

Chalcopyrite-stannite solid solutions (substage B):

Two optically different types of chalcopyrite, isotropic and anisotropic, occur in the Toyoha deposit (KASE, 1987). The isotropic one has an almost ideal chemical composition $CuFeS_2$, and occurs dominantly throughout the Toyoha deposit, while the anisotropic one is recognized only in deep levels of the southeastern veins. As shown in Figs. 2-A, 2-B, 3-B and 3-D, the anisotropic chalcopyrite is always associated with tin and/or indium minerals, and contains tin, indium and zinc in itself. The anisotropy is presumably due to distortion of the cell caused by these minor components. Microprobe work has identified additional two phases; stannite with slightly more chalcopyrite molecule than normal one, and an unnamed phase (CP-ST ss) whose data are plotted between chalcopyrite and stannite (Fig. 5). As well as the anisotropic chalcopyrite, this phase is distributed mainly in deep levels of the southeastern veins, and always exhibits complex intergrowth with stannite and the anisotropic chalcopyrite (Figs. 2-D, 3-F, 4-F). Its color is similar to that of stannite, but anisotropism is much stronger.

Stannite, kesterite (substage B) and hocartite (substage C):

Optical characters of stannite and kesterite are similar to those described in UYTENBOGAARDT and BURKE (1971). Comparison of the microscopic observations and chemical analyses have proved that Zn/Fe+Zn ratios of

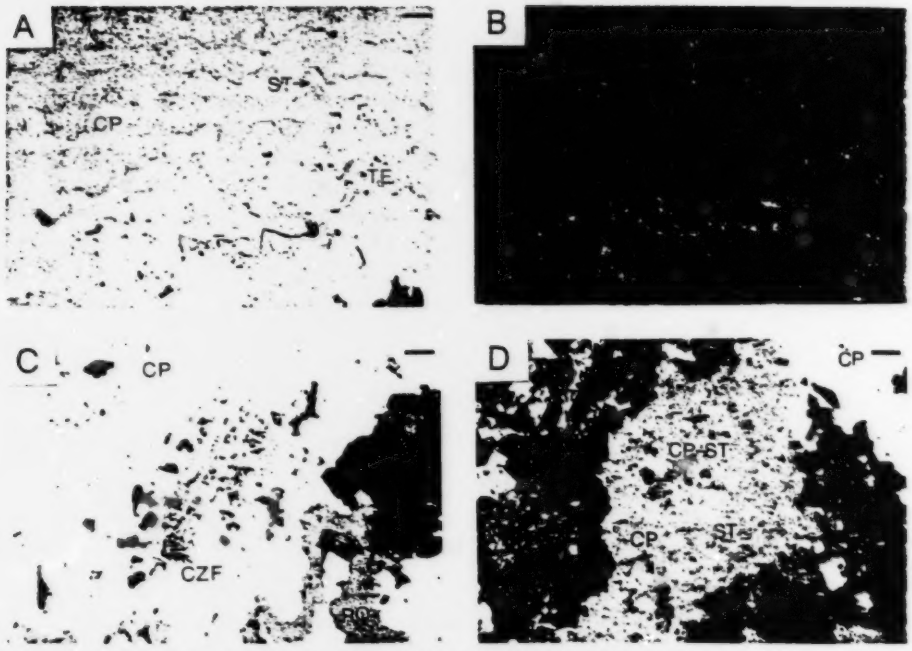

Fig. 2 Microphotographs of indium-containing minerals from Toyoha. Bars at the upper right corners of the pictures are 50 micrometers long.

2-A: Zoning of the anisotropic chalcopyrite (CP) and indium-rich stannite (ST) in the sample B409. TE: tetrahedrite.

2-B: Ditto. Crossed Nicols.

2-C: Dendritic Cu-Zn-Fe mineral (CZF) included within the anisotropic chalcopyrite (CP) from −550 meter level of the Soya vein. RQ: aggregate of roquesite, the Zn-In mineral, kesterite, and solid solutions between them.

2-D: Growth zoning of the CP-ST solid solution (CP-ST, mostly at the core) and stannite (ST). Boundaries between them are not easily recognizable in this picture. Crossed Nicols. CP: chalcopyrite, SP: sphalerite.

these minerals are negatively correlated to strength of both anisotropism and bireflectance, and to degree of brown tints. Stannite and kesterite are as common as the Zn-In mineral in the later-stage veins. Stannite dominates over kesterite at upper levels, while the amount of kesterite and maximum Zn/Fe+Zn ratios in kesterite increase downward and southeastward. At deep levels, stannite tends to coexist with the anisotropic chalcopyrite and the CP-ST ss, while kesterite occurs together with indium sphalerite and the Zn-In mineral as discrete grains or concentric parallel bands within sphalerite. As well as other silver minerals, hocartite is often observed within hydrothermally etched pits in sphalerite which includes cassiterite and/or stannite grains. This indicates that hocartite is a product of a reaction between the tin minerals of the substage B and the silver-rich hydrothermal solution of the substage C.

Roquesite and sakuraiite (substage B):

Roquesite and sakuraiite are recognized in a copper-rich ore from −550 meter level of a southern part of the Soya vein. They occur as bands or grains intergrown with kesterite and the Zn-In mineral. It is difficult to distinguish one from the other under optical microscope because these four minerals are generally mixed within a composite grain or band (Fig. 3-E). When compared with other three minerals, roquesite shows a distinct blue tint and clear

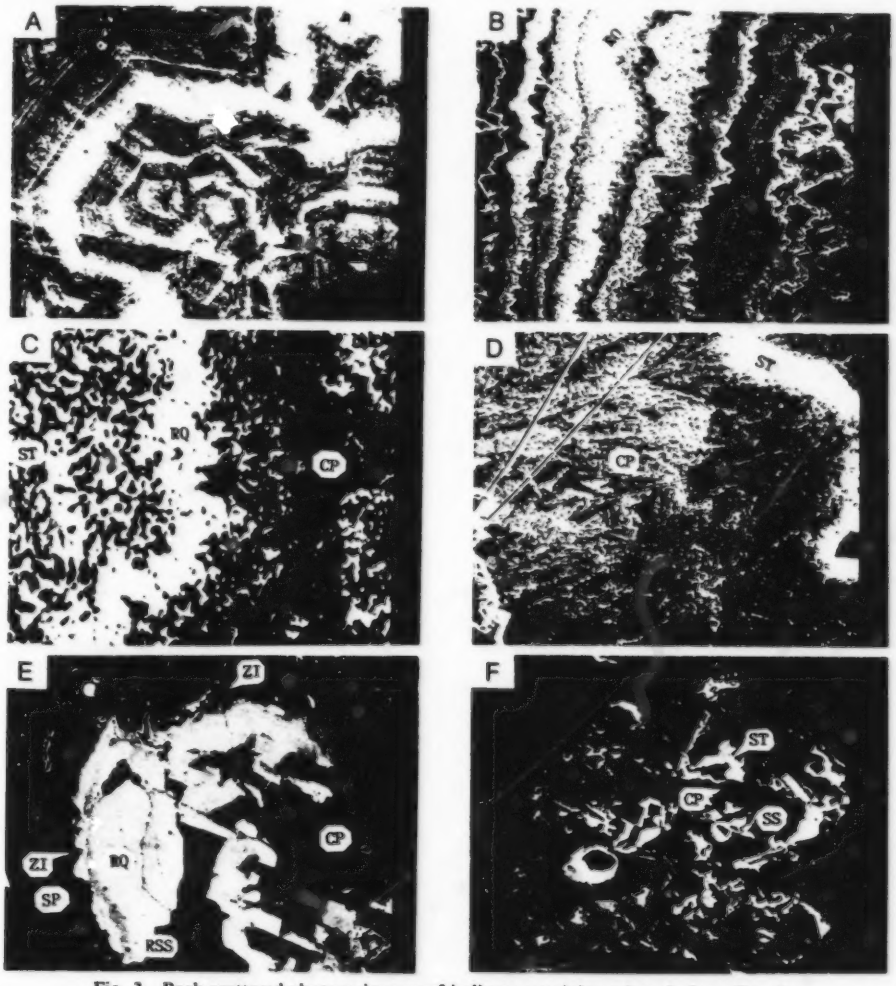

Fig. 3 Back-scattered electron images of indium-containing minerals from Toyoha.

3-A: Rhythmic zoning in sphalerite from the Sorachi vein at −350 meter level. The brighter zones contain more indium and copper (roquesite mol) than the darker zones. Sphalerite covers more than 99 percent of the the area, which corresponds to those in Figs. 4-C and 4-D.

3-B: Zoning of the anisotropic chalcopyrite, stannite, presumable roquesite, and mixtures of their fine grains in the sample B409. Black part is the anisotropic chalcopyrite, gray part is stannite. The brightest white band (RQ) is presumably of roquesite. Central part of this picture corresponds to the areas shown in Figs. 4-A and 4-B.

3-C: A part of Fig. 3-B. Note the complex mixture of chalcopyrite (CP, black), stannite (ST, gray), and roquesite (RQ, white).

3-D: The anisotropic chalcopyrite in the same section with Figs. 3-B and 3-C. Bright white bands and dots are of stannite (ST). The fingerprint-like fine patterns on chalcopyrite (CP) is presumably due to heterogeneity of minor element distribution.

3-E: Paragenesis of roquesite, the Zn-In mineral and the solid solution between them from the Soya vein at −550 meter level. Note that the Zn-In mineral (ZI, gray) is in between roquesite (RQ, white) and sphalerite (SP, dark gray), and that roquesite is in direct contact with chalcopyrite (CP, black). The boundary of roquesite to the solid solution (RSS, light gray to gray) is gradational, while that to the Zn-In mineral is sharp. The area corresponds to that in Fig. 4-E.

3-F: Intergrowth of stannite (ST), the CP-ST ss (SS) and the anisotropic chalcopyrite (CP) from the Shinano vein at −450 meter level. The area corresponds to that in Fig. 4-F.

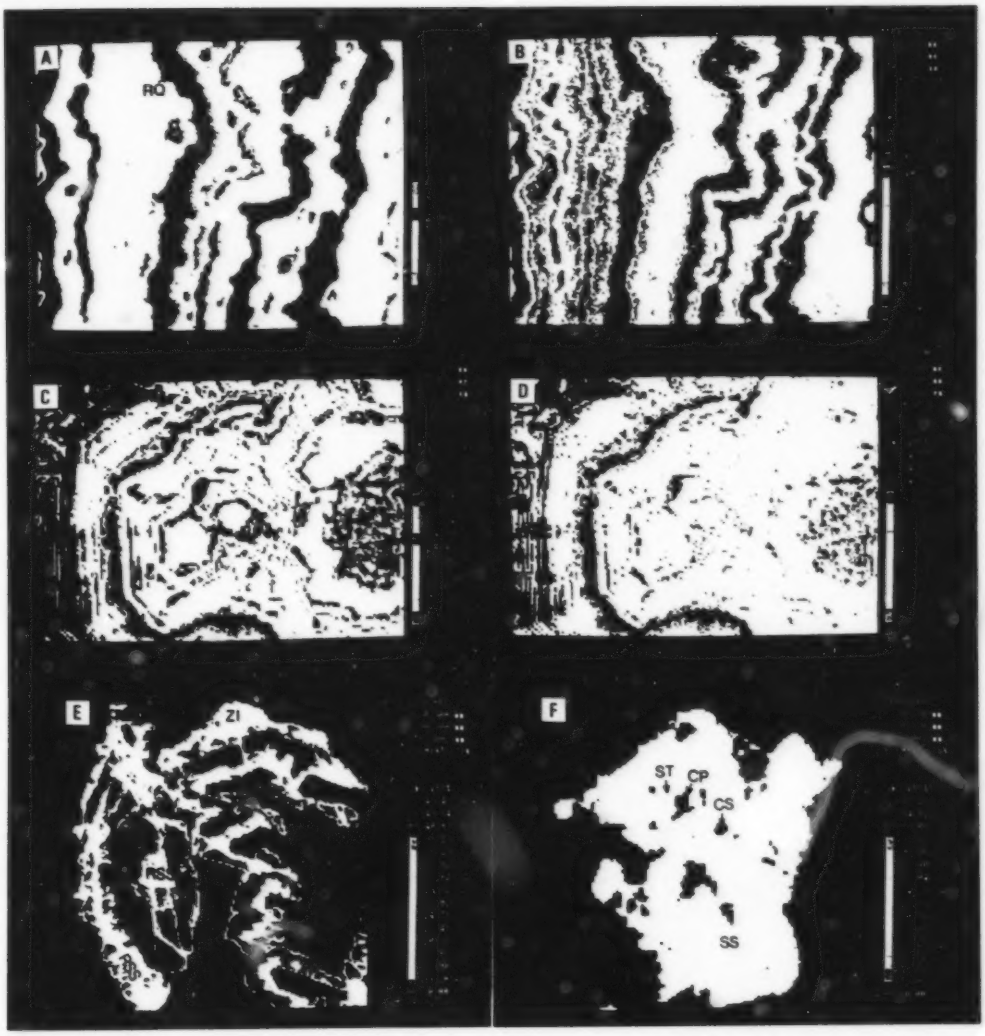

Fig. 4 Compositional maps of indium-containing minerals from Toyoha. The weight percent scales in the figures are approximate ones.

4-A: Distribution of indium in the central area shown in Fig. 3-B. The red band is presumably of roquesite with mixtures of fine-grained chalcopyrite and stannite. Bands with intermediate indium contents are of stannite with mixtures possibly of chalcopyrite and roquesite. Darkest areas correspond to the anisotropic chalcopyrite.

4-B: Distribution of tin in the same area with Fig. 4-A.

4-C: Distribution of indium in sphalerite. The area corresponds to that in Fig. 3-A.

4-D: Distribution of copper in the same area with Fig. 4-C. Note the pattern is almost identical to that of indium.

4-E: Distribution of indium in the area corresponds to that in Fig. 3-E. Note the heterogeneity in the grains due to the solid solution (RSS, light brown to light blue) between the Zn-IN mineral (ZI, light blue at the upper and left fringes of roquesite) and roquesite (RQ, brown).

4-F: Distribution of tin in an aggregate of stannite (ST, yellow), the CP-ST ss (SS, light blue) and the anisotropic chalcopyrite (CP, dark blue). The red grain at the core is cassiterite (CS). The area corresponds to that in Fig. 3-F (turned about ninety degree).

boundaries against them in some occasions, but in other occasions, the boundaries are almost invisible under microscope. In the latter case, the roquesite is actually a solid solution with composition close to that of the Zn–In mineral and sakuraiite as is described later. Moreover, the colors of kesterite and sakuraiite resemble that of the Zn–In mineral, and it is essentially impossible to discriminate between kesterite and sakuraiite under microscope, because there is no distinct gap in chemistry between these minerals from Toyoha, like as those from the Ikuno mine (Shimizu et al. 1986). Both roquesite and sakuraiite are weakly anisotropic, and show neither bireflectance nor internal reflection. Thin layers possibly of roquesite mixed with extremely fine grains of the anisotropic chalcopyrite and indium-rich stannite (Figs. 3-B, 4-A, 4-B) are recognized also in a piece of drill core named B409–113.7 m (referred to as sample B409 in the following text). Locality of the core corresponds to −350 meter level of the Shinano vein. It is notable that roquesite is observed only in chalcopyrite-rich ore, and generally in direct contact with the Zn–In mineral, kesterite or chalcopyrite, but rarely with sphalerite (Fig. 3-E), while the Zn–In mineral is widely distributed in sphalerite. This fact indicates that the assemblage roquesite-sphalerite is not stable at least in the formation conditions of the Toyoha deposit.

Cu–Zn–Fe mineral (substage B):

This unnamed phase, newly found in this study, is recognized in a polished sample from −550 meter level of the Soya vein. This strongly anisotropic phase occurs as dendrites completely included within the anisotropic chalcopyrite (Fig. 2-C) associated with roquesite, kesterite, sakuraiite, sphalerite and the Zn–In mineral. Its color is brownish gray with a violet tint, and pleochroism is not recognized.

Chemistry of Minerals

Analytical procedure:

Shimadzu EPMA-8705 (and its old model XMA-2 for some of the data) with X-ray take off angle 52.5 degrees has been employed to get chemical data and back-scattered electron images of the indium-containing minerals. Accelerating voltage and sample current for the quantitative analyses are 20 kV and 10 to 20 nA on the MgO standard. Several points for each mineral described below were qualitatively analyzed. Characteristic X-rays were selected in accordance with the result, and measured; CuKα, AgLα, FeKα, ZnKα, InLα, SnLα and SKα for all points; PbMα for berndtite and herzenbergite; SbLα and AsLα for tetrahedrite; MnKα and CdLα for some points on sphalerite and the CP-ST ss, and ZAF—atomic number (Z), absorption (A) and fluorescence (F)— corrections were made. Standards are pure metals (for Ag, Cd, Mn, Sb, Sn, and Zn), chalcopyrite (Cu, Fe, S), galena (Pb), synthetic GaAs (As) and synthetic InP (In). Though a pure metal standard of indium was used instead of InP for some of the analyses, no significant difference in the results is recognized. More than three hundred and seventy points have been analyzed in this manner, and about three hundred data which total in the range of 100±1 weight percent are employed in this report. However, additional ten data which do not total in the range are also employed especially to make the diagrams because of their unique compositions.

Minerals containing indium as minor element:

Boorman and Abbott (1967) present that weight percentages of indium in chalcopyrite, sphalerite and tetragonal stannite associated with roquesite from Mount Pleasant, New Brunswick, Canada is 0.19, 1.25 and 2.10 respectively. Picot and Pierrot (1963) describe the first occurrence of roquesite as inclusions within bornite from the Charrier mine, France. They have revealed that maximum indium concentration of sphalerite inclusions in the bornite is 0.8 weight percent. Sphalerite from the Deputatskoe deposit, USSR, contains 0.31 weight percent indium at maximum (Vlasov, 1966). The minerals from Toyoha contain the same order or more of indium. Representative EPMA analysis data of chalcopyrite are listed in Table 2. Though some points on the anisotropic chalcopyrite in the sample B409 apparently contain as much as three weight percent indium, measured indium contents in chalcopyrite from other localities in Toyoha do

Table 2 Representative chemical compositions of chalcopyrite (CP) and the Cu-Zn-Fe (CZF) mineral from Toyoha. See Table 6 for abbreviations

No	Locality	Name	Cu	Ag	Fe	Zn	In	Sn	S	Total
1	B409	CP	33.51	0.17	25.73	0.74	1.74	3.48	34.35	99.72
	atoms		1.99	0.01	1.74	0.04	0.06	0.11	4.05	8
2	B409	CP	34.09	0.09	27.42	0.25	0.89	2.43	34.52	99.69
	atoms		2.01	0.00	1.84	0.01	0.03	0.08	4.03	8
3	SR350	CP	34.61	0.11	28.91	0.77	0.39	0.34	34.55	99.70
	atoms		2.02	0.00	1.92	0.04	0.01	0.01	3.99	8
4	SY550	CP	34.33	0.13	29.44	0.29	0.34	0.23	34.96	99.72
	atoms		1.99	0.01	1.95	0.02	0.01	0.01	4.02	8
5	SR350	CP	34.08	0.09	28.72	1.63	0.30	0.41	34.34	99.56
	atoms		1.99	0.00	1.91	0.09	0.01	0.01	3.98	8
6	SN450	CP	34.32	0.10	27.33	0.49	0.07	2.99	34.13	99.44
	atoms		2.03	0.00	1.84	0.03	0.00	0.10	4.00	8
7	SY550	CZF	6.47	0.14	9.75	49.28	0.56	0.12	33.67	99.99
	atoms		0.39	0.01	0.67	2.89	0.02	0.00	4.02	8
8	SY550	CZF	7.42	0.05	9.59	49.00	0.50	0.12	33.91	100.59
	atoms		0.44	0.00	0.65	2.85	0.02	0.00	4.03	8
9	SY550	CZF	8.28	0.08	10.76	47.05	0.31	0.08	33.83	100.39
	atoms		0.50	0.00	0.73	2.74	0.01	0.00	4.02	8

Table 3 Representative chemical compositions of the Ag-In mineral (AI), hocartite (HC), berndtite (BD), herzenbergite (HZ), and rhodostannite (RS) from Toyoha. See Table 6 for other abbreviations

No	Locality	Name	Cu	Ag	Fe	Zn	In	SN	S	Pb	Total
1	SR300	AI	0.52	37.48	0.18	1.31	39.19	0.00	21.49	n.a.	100.17
	atoms		0.05	2.00	0.02	0.12	1.96	0.00	3.86		8
2	SR300	AI	0.80	36.28	0.24	1.37	39.18	0.00	21.74	n.a.	99.61
	atoms		0.07	1.93	0.03	0.12	1.96	0.00	3.89		8
3	SR300	AI	0.82	37.86	0.17	0.95	38.40	0.00	21.32	n.a.	99.52
	atoms		0.08	2.03	0.02	0.08	1.94	0.00	3.85		8
4	SR400	HC	0.42	41.22	7.33	2.69	0.14	23.44	23.92	n.a.	99.15
	atoms		0.04	2.03	0.70	0.22	0.01	1.05	3.96		8
5	SR400	HC	0.29	41.56	7.48	3.32	0.00	23.59	24.31	n.a.	100.55
	atoms		0.02	2.01	0.70	0.27	0.00	1.04	3.96		8
6	SR400	BD	0.00	0.00	1.08	0.40	0.16	63.15	34.59	0.65	100.03
	atoms		0.00	0.00	0.04	0.01	0.00	0.97	1.97	0.01	3
7	SR400	HZ	0.03	3.08	1.36	0.00	0.06	75.31	20.39	0.65	99.88
	atoms		0.00	0.12	0.15	0.00	0.00	3.85	3.86	0.02	8
8	SR400	HZ	0.00	0.58	0.55	0.09	0.00	78.98	20.17	0.00	100.38
	atoms		0.00	0.03	0.06	0.01	0.00	4.06	3.84	0.00	8
9	SR450	RS	13.19	3.69	5.90	2.28	0.18	44.92	29.91	n.a.	100.07
	atoms		1.71	0.28	0.87	0.29	0.01	3.13	7.71		14
10	SR450	RS	13.14	3.73	6.08	1.96	0.16	44.96	30.10	n.a.	100.12
	atoms		1.70	0.28	0.90	0.25	0.01	3.12	7.74		14

not exceed 0.4 weight percent. Such high indium contents in the former chalcopyrite may be partly attributed to mixtures of extremely fine-grained indium-rich stannite/kesterite and roquesite in chalcopyrite (Figs. 3-C, 3-D). However, careful checks of the sample B409 with high magnification back-scattered electron images proved that chalcopyrite in the sample definitely contains more than one weight percent indium and three weight percent tin at their maximums. It is notable that all data of the anisotropic chalcopyrite are plotted on the chalcopyrite-stannite tie line in Fig. 5. Representative chemical compositions of hocartite and rhodostannite are shown in Table 3. Maximum indium contents of hocartite and rhodostannite are 0.14 (in 26 analyses) and 0.28 (4 analyses) weight percent respective-

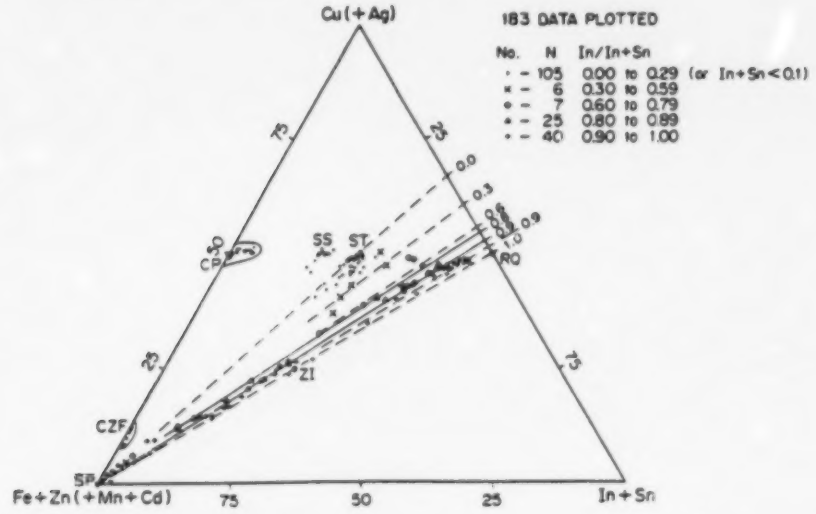

Fig. 5 Cu−Fe+Zn−In+Sn diagram of the CSR group minerals from Toyoha. Solid lines in the diagram are isovalue lines of observed In/In+Sn, and broken lines are of calculated In/In+Sn assuming that Fe^{+3} is zero. CP: chalcopyrite, SS: the CP-ST ss, ST: stannite, RQ: roquesite, ZI: Zn-In mineral, SP: sphalerite, CZF: Cu-Zn-Fe mineral. Small open circles by the abbreviations in the figure are at ideal compositions of corresponding phases. Addition of minor Ag to Cu and Mn+Cd to Fe+Zn does not make any recognizable difference on this diagram. Dots around the CZF mineral and chalcopyrite include data which exhibit less that 0.1 In+Sn in 8 total atoms. Though their In/In+Sn are not necessarily in the range from 0.00 to 0.29, the ratio for those with such low In+Sn is beyond the scope of this discussion. CSR: chalcopyrite-sphalerite-roquesite.

ly. The Ag/Cu+Ag atomic ratios in hocartite are between 0.98 and 1.00. Toyohaite (YAJIMA et al. in prep.), a newly confirmed silver analogue of rhodostannite, contains less than 0.41 weight percent indium. Measured indium concentrations in herzenbergite, berndtite, teallite, and tetrahedrite from Toyoha are very low in general, and their maximum values are 0.18 (in 8 analyses), 0.16 (6 analyses), 0.21 (12 analyses), and 0.08 (78 analyses) weight percent respectively. As Table 2 shows, indium contents in the Cu-Zn-Fe mineral are between 0.31 and 0.72 weight percent (5 analyses). Chemical compositions of the Cu-Zn-Fe mineral are intermediate of chalcopyrite and sphalerite, and close to $0.5CuFeS_2+3(Zn, Fe)S$, where the atomic ratios Fe/Zn in the sphalerite mol is approximately 0.1. This phase resembles the cuprian sphalerite described by CLARK and SILLITOE (1970), and is probably a metastable phase which has exsolved from the zinc-containing intermediate solid solution of CuS and FeS, because the observed maximum solubility of copper in the sphalerite phase between 300 and 500°C is only 1.6 weight percent (SHIMA et al., 1982; KOJIMA and SUGAKI, 1984).

Ag-In mineral:

The unnamed Ag-In mineral contains both silver and indium as major components (Table 3), and reveals chemical composition close to $AgInS_2$. Its Ag/Ag+Cu atomic ratios are between 0.96 and 0.98 (in 5 analyses). No crystallographical data for this mineral is obtained yet. However, those of synthetic $AgInS_2$ is well documented (e.g. ROTH et al., 1973), and comparative study might be done in the future. In chemical term, this is regarded as Ag analogue of roquesite.

Zn-In mineral and sphalerite:

Normal sphalerite generally contains less than 0.3 weight percent indium and optically homogeneous, but indium sphalerite associated with the Zn-In mineral often shows rhyth-

Table 4 Representative chemical compositions of solid solution between sphalerite and the Zn-In mineral.

No	Locality	Name	Cu	Ag	Fe	Zn	In	SN	S	Mn	Cd	Total
1	SY550	ZI	15.25	0.26	1.28	29.44	22.73	2.66	28.91	n.a.	n.a.	100.53
	atoms		1.05	0.01	0.10	1.96	0.86	0.10	3.93			8
2	SY550	ZI	14.57	0.25	2.26	30.31	21.06	2.22	29.14	n.a.	n.a.	99.81
	atoms		0.99	0.01	0.18	2.01	0.80	0.08	3.94			8
3	SY550	ZI	12.41	0.21	3.74	33.99	17.88	2.30	29.50	n.a.	n.a.	100.03
	atoms		0.83	0.01	0.29	2.21	0.66	0.08	3.92			8
4	SR350	ZI	9.96	0.20	1.53	40.54	15.89	1.25	30.43	n.a.	n.a.	99.80
	atoms		0.66	0.01	0.12	2.60	0.58	0.04	3.99			1.90
5	SR350	ZI	9.15	0.26	1.80	42.49	13.99	1.47	30.72	n.a.	n.a.	99.87
	atoms		0.60	0.01	0.14	2.71	0.51	0.05	3.99			1.92
6	SR350	ZI	9.15	0.12	2.41	43.88	10.85	2.42	31.12	n.a.	n.a.	99.97
	atoms		0.59	0.01	0.18	2.76	0.39	0.08	3.99			1.95
7	SR350	SP	7.51	0.16	2.71	48.40	8.86	1.74	31.09	n.a.	n.a.	100.46
	atoms		0.48	0.01	0.20	3.01	0.31	0.06	3.94			8
8	IZ400	SP	4.16	0.41	7.24	48.02	6.98	0.36	32.30	0.06	0.69	100.22
	atoms		0.26	0.01	0.52	2.92	0.24	0.01	4.01	0.00	0.03	8
9	SY550	SP	3.00	0.05	3.07	56.71	4.73	0.46	32.61	n.a.	n.a.	100.63
	atoms		0.19	0.00	0.22	3.42	0.16	0.02	4.00			8
10	SR350	SP	2.29	0.70	1.27	61.40	1.62	0.46	32.42	0.00	0.00	100.15
	atoms		0.14	0.03	0.09	3.70	0.06	0.01	3.98	0.00	0.00	8
11	IZ400	SP	0.79	0.11	5.80	58.01	0.68	0.32	33.02	0.05	0.49	99.26
	atoms		0.05	0.00	0.41	3.47	0.02	0.01	4.02	0.00	0.02	8
12	SY550	SP	0.56	0.04	0.84	65.30	0.09	0.32	33.15	n.a.	n.a.	100.30
	atoms		0.03	0.00	0.06	3.88	0.00	0.01	4.02			8
13	SR350	SP	0.53	0.19	3.86	62.13	0.09	0.08	32.85	0.00	0.00	99.72
	atoms		0.03	0.01	0.27	3.70	0.00	0.00	3.99	0.00	0.00	8
14	SN450	SP	0.44	0.00	0.95	65.06	0.04	0.14	33.02	0.03	0.05	99.74
	atoms		0.03	0.00	0.07	3.88	0.00	0.01	4.01	0.00	0.00	8

ZI:Zn-In mineral and the solid solution with less than 50 percent sphalerite mol, SP:sphalerite and the solid solution with more than 50 percent sphalerite mol. See Table 6 for other abbreviations.

mic zoning easily recognizable under optical microscope. Distribution maps of copper and indium in Figs. 4-C and 4-D evidently show that the zoning is due to these elements proportionally distributed in sphalerite. Average weight percentages of indium and copper in the mapped area are calculated to be 2.5 and 1.6 respectively. This gives Cu/In atomic ratio around 1.1, and is in good agreement with the quantitative analysis of indium sphalerite which are plotted to the upper side of the roquesite-sphalerite tie line in Fig. 5. As Table 4 and Fig. 5 show, the solid solution between sphalerite and the Zn-In mineral seems to be complete. An extensive solid solution is recognized also between roquesite and the Zn-In mineral. All these facts indicate that indium is very soluble in sphalerite as roquesite ($CuInS_2$) mol, and that the crystal structure of the Zn-In mineral is similar to that of roquesite or sphalerite. The synthetic $CuZn_2InS_4$ has sphalerite structure (Parthe et al., 1969; Kissin and Owens, 1986). However, weak anisotropism occasionally observed in the Zn-In mineral is inconsistent with the cubic sphalerite structure. Therefore the structure of the Zn-In mineral is not easily determined, but is probably close to that of sphalerite.

Roquesite:

Representative analysis data of roquesite (RQ) and its solid solution with the Zn-In mineral (ZI) are listed in Table 5. They are plotted to the stannite (ST) side of the ZI-RQ tie line in Fig. 5. The zinc-rich end of the RQ-ZI solid solution is close to sakuraiite which data are plotted to the roquesite side of the ST-ZI tie line. The range of the solid solution is from $RQ_{90}ZI_{10}$ to $RQ_{37}ZI_{63}$ when kesterite mol is neglected. A wide variation in the composition between $RQ_{90}ZI_{10}$ and $RQ_{49}ZI_{51}$ is

Table 5 Representative chemical compositions of solid solutions among roquesite, kesterite and the Zn-In mineral from Toyoha.

No	Locality	Name	Cu	Ag	Fe	Zn	In	Sn	S	Total
1	SY550	RQ	24.68	0.92	0.38	2.44	42.68	2.16	26.07	99.33
	atoms		1.89	0.04	0.03	0.18	1.81	0.09	3.96	8
2	SY550	RQ	24.60	0.97	1.77	3.07	41.11	1.89	26.53	99.94
	atoms		1.85	0.04	0.15	0.22	1.71	0.08	3.95	8
3	SY550	RQ	23.84	0.68	0.78	6.63	37.88	3.31	27.19	100.31
	atoms		1.76	0.03	0.07	0.48	1.55	0.13	3.98	8
4	SY550	RQ	23.24	0.45	1.54	8.66	33.20	4.96	27.63	99.68
	atoms		1.70	0.02	0.13	0.62	1.34	0.19	4.00	8
5	SY550	RQ	21.76	0.49	1.04	11.95	34.54	2.38	27.77	99.93
	atoms		1.58	0.02	0.09	0.84	1.39	0.09	3.99	8
6	SY550	RQ	22.48	0.47	2.40	12.77	27.79	6.27	27.98	100.16
	atoms		1.61	0.02	0.20	0.89	1.10	0.24	3.96	8
7	SY550	RQ	21.84	0.42	1.37	16.03	25.37	7.06	27.85	99.94
	atoms		1.56	0.02	0.11	1.11	1.00	0.27	3.93	8
8	SY550	KS	21.92	0.23	3.90	18.00	16.34	12.57	28.72	101.68
	atoms		1.50	0.01	0.30	1.20	0.62	0.46	3.90	8
9	SY550	KS	23.63	0.28	3.87	15.76	11.98	16.32	29.07	100.91
	atoms		1.62	0.01	0.30	1.05	0.46	0.60	3.96	8
10	SR350	KS	25.48	0.26	3.65	17.05	1.83	21.91	29.33	99.52
	atoms		1.74	0.01	0.28	1.13	0.07	0.80	3.97	8
11	SR350	KS	26.47	0.34	3.14	15.03	0.32	25.97	28.63	99.89
	atoms		1.83	0.01	0.25	1.01	0.01	0.96	3.92	8
12	SR450	KS	25.66	1.57	4.84	12.12	1.86	25.98	28.13	100.16
	atoms		1.79	0.06	0.38	0.82	0.07	0.97	3.89	8
13	SY550	KS	27.44	0.33	4.93	9.94	6.71	22.84	28.49	100.68
	atoms		1.90	0.01	0.39	0.67	0.26	0.85	3.92	8
14	SR350	KS	27.66	0.43	4.52	12.00	1.15	25.87	28.79	100.44
	atoms		1.90	0.02	0.35	0.80	0.04	0.95	3.93	8
15	B409	KS	28.96	0.24	6.11	9.24	0.14	25.98	29.22	99.89
	atoms		1.98	0.01	0.48	0.61	0.01	0.95	3.96	8

RQ:roquesite and solid solutions between the Zn-In mineral and roquesite, KS:kesterite and solid solutions between the Zn-In mineral and kesterite (sakuraiite). See Table 6 for other abbreviations.

recognized even within a single grain shown in Figs. 3-E and 4-E. The compositional gap recognized between the solid solution and the Zn-In mineral is indicated also by the sharp boundary between them on the back-scattered electron image (Fig. 3-E). Some data plotted at the midst of roquesite and stannite (Figs. 5, 8) are of the fine-grained mixtures in the sample B409 (Fig. 3-C). The mixtures are presumably of roquesite and indium-rich stannite or kesterite.

Stannite, kesterite and sakuraiite:

Results of the EPMA analyses of stannite and kesterite are shown in Tables 5 and 6. Sakuraiite can be considered as a solid solution of kesterite and the Zn-In mineral. Some data which correspond to compositions of sakuraiite are plotted between kesterite and the Zn-In mineral. Observed highest mol ratio of the Zn-In mineral to kesterite among them is 70 to 30. Observed variation in Zn/Fe+Zn of stannite and kesterite from Toyoha is between 0.09 and 0.94, and no definite gap is recognized in it. Though stannite and kesterite are structurally distinct (HALL et al., 1978), Zn/Fe+Zn atomic ratios can be high up to 0.55 in stannite, and be as low as 0.45 in kesterite (PETRUK, 1973). Consequently, chemical compositions are useless to discriminate between the two if the ratio is in the range from 0.45 to 0.55. Strict discrimination, however, is not needed in the following discussion, therefore the name 'kesterite' is used for those in which Zn/Fe+Zn are larger than 0.5. Weight percent range of indium contents in stannite is 0.04 to 9.85 for 25 points ex-

Table 6 Representative chemical compositions of stannite (ST), the CP-ST ss (SS), and the mixtures of fine-grained stannite/kesterite and roquesite (MKR) from Toyoha.

No	Locality	Name	Cu	Ag	Fe	Zn	In	SN	S	Mn	Cd	Total
1	SR350	ST	29.19	0.20	7.47	6.76	1.01	26.93	28.74	n.a.	n.a.	100.31
	atoms		2.01	0.01	0.58	0.45	0.04	0.99	3.92			8
2	IZ500	ST	26.97	0.30	8.52	6.49	0.78	26.89	29.59	n.a.	n.a.	99.54
	atoms		1.85	0.01	0.67	0.43	0.03	0.99	4.02			8
3	SN450	ST	28.89	0.05	10.35	5.47	0.49	25.32	29.30	n.a.	n.a.	99.88
	atoms		1.96	0.00	0.80	0.36	0.02	0.92	3.94			8
4	SN450	ST	28.75	0.02	10.10	6.49	0.42	25.76	29.04	n.a.	n.a.	100.57
	atoms		1.95	0.00	0.78	0.43	0.02	0.93	3.90			8
5	SR450	ST	27.95	0.66	7.62	6.11	0.11	28.22	29.20	n.a.	n.a.	99.87
	atoms		1.93	0.03	0.60	0.41	0.00	1.04	3.99			8
6	IZ300	ST	28.26	0.00	9.24	6.76	0.00	25.89	29.48	n.a.	n.a.	99.63
	atoms		1.92	0.00	0.72	0.45	0.00	0.94	3.97			8
7	SY550	ST	25.42	0.29	8.61	8.33	9.85	19.70	28.27	n.a.	n.a.	100.47
	atoms		1.76	0.01	0.68	0.56	0.38	0.73	3.88			8
8	B409	ST	30.67	0.18	15.01	2.86	6.22	15.01	30.32	n.a.	n.a.	100.27
	atoms		2.01	0.01	1.12	0.18	0.23	0.53	3.93			8
9	B409	ST	28.21	0.20	8.09	9.35	5.90	19.12	29.98	n.a.	n.a.	100.85
	atoms		1.89	0.01	0.62	0.61	0.22	0.69	3.98			8
10	SN450	SS	28.37	0.14	12.72	8.29	0.24	20.06	30.64	0.03	0.11	100.60
	atoms		1.85	0.01	0.94	0.53	0.01	0.70	3.96	0.00	0.00	8
11	SN450	SS	28.97	0.14	12.94	8.00	0.20	18.77	30.89	0.03	0.11	100.04
	atoms		1.88	0.01	0.96	0.51	0.01	0.65	3.98	0.00	0.00	8
12	SN450	SS	30.04	0.14	14.42	5.19	0.08	19.81	30.50	0.02	0.11	100.32
	atoms		1.96	0.01	1.07	0.33	0.00	0.69	3.94	0.00	0.00	8
13	B409	MKR	27.43	0.30	5.26	2.80	26.11	11.05	26.74	n.a.	n.a.	99.70
	atoms		2.00	0.01	0.44	0.20	1.05	0.43	3.87			8
14	B409	MKR	28.99	0.37	8.14	3.03	16.35	14.26	28.58	n.a.	n.a.	99.72
	atoms		2.02	0.02	0.65	0.21	0.63	0.53	3.95			8

SR: Sorachi vein, IZ: Izumo vein, SN: Shinano vein, SY: southern Soya vein, B409: the sample B409 (corresponds to -350 meter level of Shinano vein). n.a.: not analyzed. Numbers immediately after the vein name abbreviations indicate levels (depth in meters).

cept those in the sample B409, in which indium contents of the stannite bands (Figs. 3-B, 4-A, 4-C) reach up to 20.0 weight percent. This may be partly attributed to evenly mixed roquesite and chalcopyrite grains; not to roquesite grains only, because even those points plotted to the chalcopyrite side of ST on Fig. 5 contain as high as 14.5 weight percent indium. The indium content of kesterite ranges from 0.11 to 1.86 weight percent (14 analyses) in the Sorachi vein between −200 and −450 meter levels, and 5.90 to 16.51 (4 analyses) in the Soya vein at −550 meter level and in the sample B409. In/In+Sn atomic ratios also vary widely from 0.00 to 0.57. In short, kesterite, sakuraiite and stannite associated with roquesite are very rich in indium, and are all plotted to the roquesite side of the ST-ZI tie line on Fig. 5.

Discussions

Minerals as indium carriers:

Indium contents of herzenbergite, berndtite, teallite, rhodostannite, toyohaite, and hocartite are low as already described, and the Ag-In mineral is quite rare. Therefore these minerals are negligible as indium carriers in economic sense. Probably more than 99 percent of indium in Toyoha is concentrated in the Zn-In mineral, sphalerite, stannite, kesterite, sakuraiite, roquesite and the anisotropic chalcopyrite. As all of these minerals and the Cu-Zn-Fe mineral are composed mainly of Cu, Fe, Zn, In, Sn and S, and plotted within the chalcopyrite-sphalerite-roquesite triangle in Fig. 5, they are expressed as CSR group minerals in the following discussion. They have 1:1 metal to sulfur ratio, and

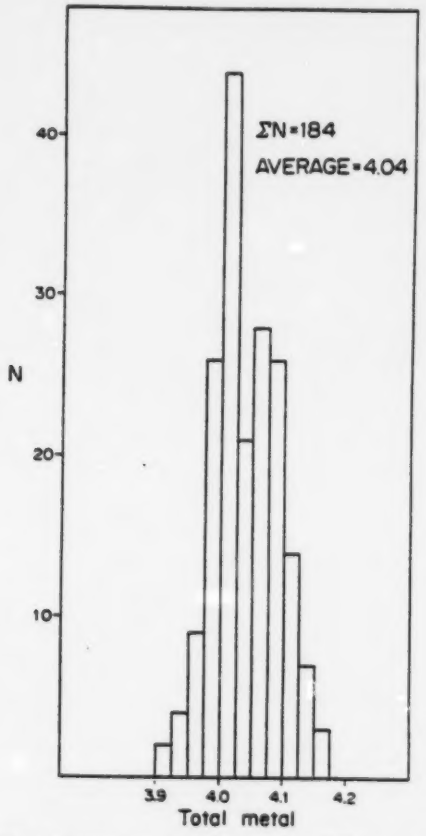

Fig. 6 Histogram of total metal on the basis of 8 total atoms calculated from the analysis for the CSR group minerals and hocartite.

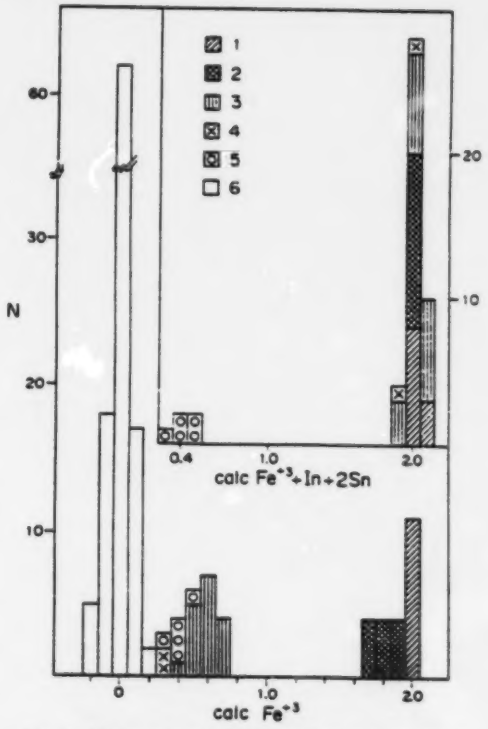

Fig. 7 Histogram of calculated Fe^{+3} and calculated $Fe^{+3}+In+2Sn$ for the CSR group minerals. Actually the latter equals to Cu+Ag. 1: normal chalcopyrite, 2: anisotropic chalcopyrite, 3: The CP-ST ss and the mixtures of stannite and the anisotropic chalcopyrite in the sampel B409, 4: indium-rich stannite and kesterite in the sample B409, 5: the Cu-Zn-Fe mineral, 6: stannite, kesterite, roquesite, sphalerite and the Zn-In mineral. The $Fe^{+3}+In+2Sn$ histogram is for only those with Fe^{+3} higher than 0.25.

belong to tetragonal or cubic crystal system, provided that the Zn-In mineral is either cubic or tetragonal as discussed in the preceding chapter. Valences of metals in these minerals are considered to be +1 for Cu and Ag, +2 for Zn, +3 for In, +4 for Sn, and +2 and +3 for Fe (e.g. KATO, 1974). With this assumption, the ideal chemical formula common for the CSR group minerals is expressed as:

$$(Cu, Ag)_m(Zn, Fe^{+2})_d(In, Fe^{+3})_tSn_qS_4.$$

Fig. 6 shows a histogram of total numbers of the metals in the formula, m+d+t+q, for 184 analyses of the CSR group minerals and hocartite. The average (4.04) is close to the theoretical number (4.00). The slight difference is probably due to systematic error of the analysis and the ZAF correction.

Relation of Fe^{+3} and In, and element substitutions in the CSR group minerals:

Provided that the ideal formula is applicable to the CSR group minerals, following equations are obtained:

$$Cu+Ag+Fe^{+2}+Zn+Fe^{+3}+In+Sn=4 \qquad (m+d+t+q)$$

$$Cu+Ag+2(Fe^{+2}+Zn)+3(Fe^{+3}+In)+4Sn=8 \qquad \text{(total charge)}$$

therefore

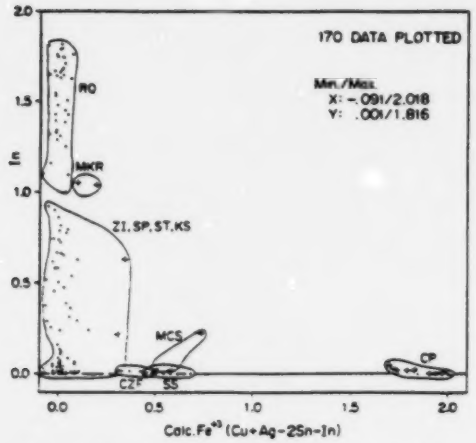

Fig. 8 Calculated Fe^{+3} vs. In diagram of the CSR group minerals. The Fe^{+3} axis corresponds to that in Fig. 7. Plus (+) marks data of the sample B409. Abbreviations are RQ: roquesite, ZI: Zn-In mineral, SP: sphalerite, ST: stannite, KS: kesterite, CZF: Cu-Zn-Fe mineral, SS: CP-ST ss, CP: chalcopyrite, MCS: mixture of chalcopyrite and stannite in the sample B409, MKR: mixture of kesterite/stannite and roquesite in the sample B409.

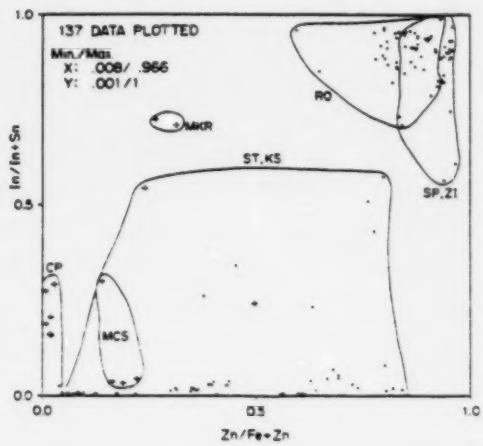

Fig. 9 Zn/Fe+Zn vs. In/In+Sn (atomic ratios) diagram of the CSR group minerals with both In+Sn and Fe+Zn value more than 0.1 (in 8 total atoms). Plus (+) marks data of the sample B409. See Fig. 8 for abbreviations.

$$Fe^{+3} = Cu + Ag - 2Sn - In$$

Fig. 7 shows a histogram of Fe^{+3} for these minerals calculated by means of this equation. As is expected, the data for stannite, kesterite, sphalerite, roquesite, and the Zn-In mineral make a sharp peak at 0.0 Fe^{+3}, and data of optically normal chalcopyrite concentrate at 2.0 Fe^{+3}. The anisotropic chalcopyrite exhibits Fe^{+3} between 1.65 and 1.95, the Cu-Zn-Fe mineral between 0.25 and 0.55, and two data of anomalously indium-rich stannite and kesterite in the sample B409 between 0.25 and 0.35. The ranges for the CP-ST ss and for the mixtures of stannite and chalcopyrite in the sample B409 are almost same; between 0.35 and 0.75. Fig. 7 shows also that minerals with Fe^{+3} higher than 0.25 except the Cu-Zn-Fe mineral make a peak at 2.0 of $Fe^{+3} + In + 2Sn$, which is identical to Cu+Ag. In addition to this fact, Fig. 8 clearly shows that indium is incompatible with Fe^{+3} in all samples except the B409; the analyzed points with the calculated Fe^{+3} more than 0.25 contain less than 0.1 (in 8 total atoms) indium, and Fe^{+3} is less than 0.25 in the points which contain more than 0.1 of indium. Based on the chemical analyses, these abnormal phases plotted between normal chalcopyrite and roquesite on the Figs. 5 and 7 are attributed to three types of substitutions. For the phases plotted between normal chalcopyrite and stannite on Fig. 5, the substitution of $(Fe^{+2}, Zn)Sn$ for $2Fe^{+3}$ is dominant, and the substitution of In for Fe^{+3} is important only to the indium-rich stannite. A combination of the two, the substitution of (Fe, Zn)Sn for 2In, causes the indium-rich stannite and kesterite plotted between normal stannite and roquesite. As for the In/In+Sn atomic ratio, following equation is obtained from the above equations:

$$rc = 2c + Fe^{+3} - m$$

where r is In/Sn+In, and c represents total number of tin and indium in eight total atoms. As shown in Figs. 7 and 8, Fe^{+3} is essentially zero for the majority of those with high indium contents. If Fe^{+3} equals zero:

$$r = 2 - m/c$$

From this equation, iso-r lines for $Fe^{+3} = 0$ are put in Fig. 5, which shows that observed iso-r lines are plotted slightly to the left of the

calculated lines of the same r value. This may be attributed to the existence of minor amounts of Fe^{+3}, Mn^{+3} etc., as well as to the analytical error. A diagram of In/In+Sn versus Zn/Zn+Fe for the CSR group minerals shows positive correlation of the ratios (Fig. 9). Those data of the sample B409 are out of the trend here again. The solid solutions between sphalerite and roquesite through the Zn–In mineral are due mainly to a substitution of 2(Zn, Fe) for CuIn. The substitution of (Zn, Fe)In for CuSn recognized between kesterite and sakuraiite from the Ikuno mine (Shimizu et al., 1986) is deduced from the two substitutions already discussed, (Zn, Fe)Sn for 2In and 2(Zn, Fe) for CuIn. This substitution is recognized also in Toyoha. Obviously, a substitution of $CuFe^{+3}$ for $2(Zn, Fe^{+2})$ in sphalerite make the Cu–Zn–Fe mineral. The compositional deviations of stannite and the CP–ST ss towards sphalerite (Fig. 5) may be due to influence of adjoining sphalerite around their boundaries, or may indicate solid solutions between them. This should be left to further studies.

Estimation of equilibrium temperatures of sphalerite and stannite/kesterite:

Yajima and Ohta (1979) estimated the formation temperature range of the Izumo vein at 200 to 300°C through fluid inclusion work. However, the fluid inclusion temperatures were measured only for coarse crystals of quartz and of translucent sphalerite. Both of them are rather rare in the later-stage veins, and there is no evidence that the formation temperatures of other minerals are in the same range. With this point of view, equilibrium temperatures for some pairs of sphalerite and stannite or kesterite are calculated from their compositions by means of the Fe–Zn partitioning equations under the assumption that the equations are applicable also to the kesterite-sphalerite pair. The results are:

228(118)°C; using averaged compositions of sphalerite (8 points) and stannite (6 points) in a sample from the Shinano vein at −450 meter level.

352(319)°C; using averaged compositions of sphalerite (4 points) and kasterite (8 points) in a sample from the Sorachi vein at −350 meter level.

310(242), 350(315) and 358(331)°C; using three pairs of sphalerite and kesterite in contact with each other in a sample from the Soya vein at −550 meter level.

The values within parentheses are calculated from the equation after Nekrasov et al. (1979), and those without are after Nakamura and Shima (1982). The equations are applied only to pairs where the grains show fairly homogeneous Zn/Fe+Zn ratios, and do not contain much elements, such as indium, which are not in the experimented system. The equation of Nekrasov et al. gives unreasonably low temperature for the pair from the Shinano vein, and, therefore, that of Nakamura and Shima should be employed here. Such small number of data can not be representatives of averaged formation temperatures of the veins by any means, but suggest that peak temperatures were significantly higher than 300°C at the substage of tin-indium mineralization.

Phases as evidences for high formation temperatures:

The concentric parallel bands of indium-containing chalcopyrite, indium-rich stannite/kesterite, roquesite and mixtures of their extremely fine grains (Figs. 3–B, 3–C, 3–D) in the sample B409 can not simply be considered as normal aggregates of these minerals. All the analysis data of these minerals and their mixtures are plotted on the chalcopyrite-roquesite tie line in Fig. 5, which is consistent with the microscopic observation that even a piece of other mineral is not recognized in these bands. Besides, the mixtures are not recognized in normal stannite nor in normal chalcopyrite. These features indicate that the mixture in Fig. 3–C is not a product of precipitation of such fine-grained minerals nor of replacement. Therefore, the formation of the mixture might be attributed to exsolution of a series of zoned intermediate solid solutions between indium-rich stannite and chalcopyrite, and between stannite/kesterite and roquesite. Though existence of a wide-range solid solution of the latter pair has not been reported yet, the abnormal data of the mixtures in the sample B409

plotted in Figs. 8 and 9 indicate that wide-range solid solutions exist between $CuFeS_2$ and $CuInS_2$ by the combined substitutions of In for Fe^{+3} and of $2Fe^{+3}$ for $(Fe^{+2}, Zn)Sn$. Some data for indium-rich stannite and kesterite plotted to the right of normal stannite composition in Fig. 5 are consistent to this hypothesis. Experimental data for the chalcopyrite-stannite solid solutions (Ohtsuki et al., 1980, 1982) show that an assemblage of tin-poor stannite and an intermediate solid solution is stable in sulfur-poor conditions at 400°C. Tin contents of the stannite are as low as 11 atomic percent (Sn 0.88 in 8 total atoms), and of the solid solution are 1 to 3.3 atomic percent (Sn 0.08 to 0.26). They may correspond to the CP-ST ss and the anisotropic chalcopyrite assemblage. In any case, the CP-ST ss suggests that a pulse of high temperature may have reached up to 400°C in the later-stage veins which have been formed under sulfur-poor conditions as is evidenced by the mineral assemblages (Yajima and Ohta, 1979; Ohta, 1980). Various types of rhythmic zonings are commonly recognized in the later-stage veins; for various assemblages of minerals, for indium, copper and iron contents in sphalerite, for cobalt contents in pyrite and arsenopyrite (Ohta, unpublished), for As/Sb ratios in tetrahedrite-tennantite solid solution etc. These zonings, together with the discrepancy between the fluid inclusion data and the Fe-Zn partitioning temperatures, suggest that the later-stage veis have been formed by pulsatile mineralization which peak temperatures were high enough to form the solid solutions and the mixtures described above.

Conclusions

On the basis of the above results and discussions, it is concluded that:

(1) Economically most important indium carriers in the Toyoha deposit are the Zn-In mineral and indium sphalerite distributed in the later-stage veins. Next important are kesterite, stannite and the anisotropic chalcopyrite.

(2) The indium sphalerite is proved to be a solid solution between normal sphalerite and the Zn-In mineral. Observed continuous solid solutions between $RQ_{90}ZI_{10}$ and $RQ_{37}ZI_{63}$, between $KS_{100}ZI_0$ and $KS_{30}ZI_{70}$, and between $ZI_{100}SP_0$ and ZI_0SP_{100} are attributed to coupled substitutions of 2(Zn, Fe) for CuIn and of (Zn, Fe)In for CuSn. Other dominant substitutions recognized are of $(Fe^{+2}, Zn)Sn$ for $2Fe^{+3}$ between chalcopyrite and stannite, and of $(Fe^{+2}, Zn)Sn$ for 2In between stannite/kesterite and roquesite.

(3) Though indium is incompatible with Fe^{+3} in the CSR group minerals, the texture and chemical compositions of the mixtures of the anisotropic chalcopyrite, indium-rich stannite/kesterite, and roquesite in the sample B409 indicate wide-range substitution of In for Fe^{+3} at high temperatures. Therefore high indium contents in such mixtures and associated chalcopyrite are expected at deep levels of the southeastern later-stage veins.

(4) The occurrences of the Zn-In mineral and of roquesite indicate that the assemblage roquesite-sphalerite is unstable at least in the formation conditions of the Toyoha deposit.

(5) The later-stage veins are considered to have been formed by pulsatile mineralization whose peak temperatures were 50 to 100°C higher than the hitherto estimated maximum formation temperature (300°C) of the Toyoha deposit.

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豊羽鉱山におけるインジウム鉱物の産状と化学組成

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要旨：豊羽銀鉛亜鉛鉱床には錫・銅と共にインジウムが存在する．ビスマス，タングステン，アンチモン，砒素，コバルトも微量ながら広範囲に分布する．インジウム鉱物としては閃亜鉛鉱とインジウム銅鉱の中間組成を有する亜鉛インジウム鉱物，$AgInS_2$ の組成を有する銀インジウム鉱物，インジウム銅鉱，櫻井鉱が産するが，ケステライト，黄錫鉱，閃亜鉛鉱，異方性を有する黄銅鉱もかなりの量のインジウムを含む．これらのうち経済的に最も重要なのは亜鉛インジウム鉱物と含インジウム閃亜鉛鉱で，次いでケステライト，黄錫鉱，含インジウム黄銅鉱である．含インジウム閃亜鉛鉱は亜鉛インジウム鉱物と閃亜鉛鉱の固溶体であることが判明した．また，インジウム銅鉱と亜鉛インジウム鉱物，ケステライトと亜鉛インジウム鉱物それぞれの間にも広い固溶体の存在が認められた．これらの固溶体は 2(Zn, Fe) と CuIn, (Zn, Fe)In と CuSn の置換によるものである．黄銅鉱と黄錫鉱間の固溶体では $(Fe^{+2}, Zn)Sn$ と $2Fe^{+3}$，黄錫鉱またはケステライトとインジウム銅鉱間では $(Fe^{+2}, Zn)Sn$ と 2In の置換がそれぞれ主なものである．上記の鉱物の産状は，今まで見積られていた豊羽鉱床の最高生成温度(300℃)よりも50から100℃高い温度でこれらの鉱物が晶出したことを裏付ける．

APPENDIX C. SUMMARY: MINING IN TOYOHA MINE

Summary: Mining in Toyoha Mine

July,1990
(revised)

Stoping:

The mining method was cut and fill once before, but sub-level stoping has been practised since 1967.

Drifting and tunneling for exploration and stope preparation is carried out with a combination of 2-boom jumbo, and bucket loader or LHD.

According to the width of the vein , 2 to 10 parallel or fan-shaped long holes in a row are drilled downward from each sub-level drift. Down-the-hole Drill(DHD) or Fan-cut Hydraulic Drill are utilized. The hole diameter is 105~55 millimeters and blasted by AN-FO and /or emulsion explosives. The broken ore is loaded at dravpoint and hauled into ore chutes by LHD. (Fig.1, Fig.2)

The combinations of the underground equipments are as follows.

Item	Drill machine	Loading machine
Tunnel & Drift	2-boom jumbo: (F:Furukawa)PD90-MJ,TJ (Tamrock)H207-MMJ,RMJ Leg drill: (F) ASD-322	LHD:(Toro)300D (K:Kawasaki)M-6,M-7 (Wagner)ST-2P (Eimco)922D,922E Truck:(Eimco)ME985 Schaeff loader: (Kenco)KL-15,KL-7,KTL-7 Bucket loader:(T:Taikuu)#650 Tire loader:(T)TL-2,TZH
Raise	Raise borer: (Kouken)BM-40,BM-100 Stoper:(F)ASD-530	
Stope	DHD jumbo: (Ingersoll)DHD340A-CMM2 Fan-cut drill jumbo: (F) HD170-MMJ	LHD: (K)M-6,M-7,M-8

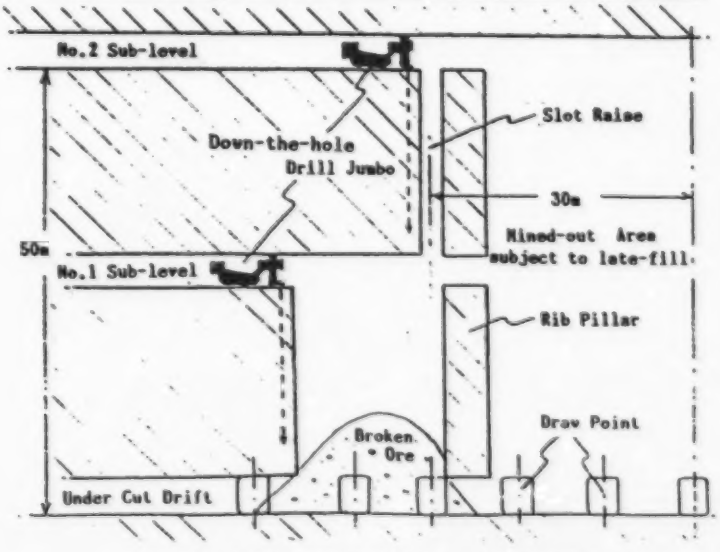
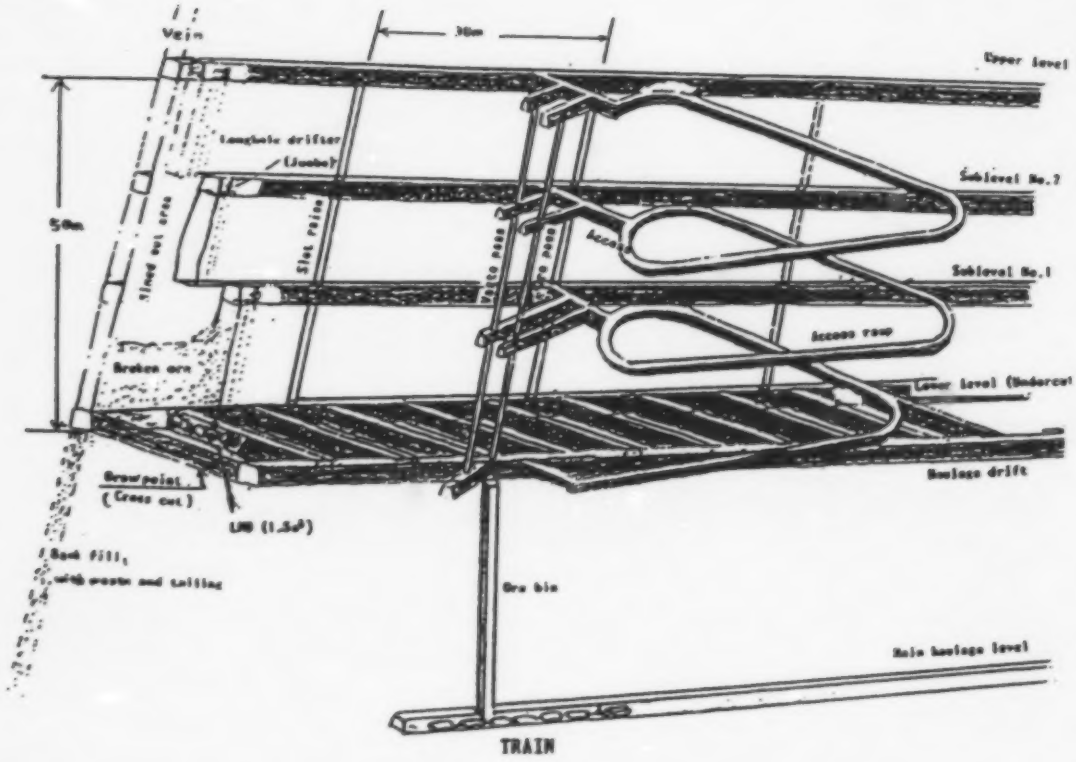


Fig. 1 Sub-level stoping layout (by DHD)



Longitudinal section

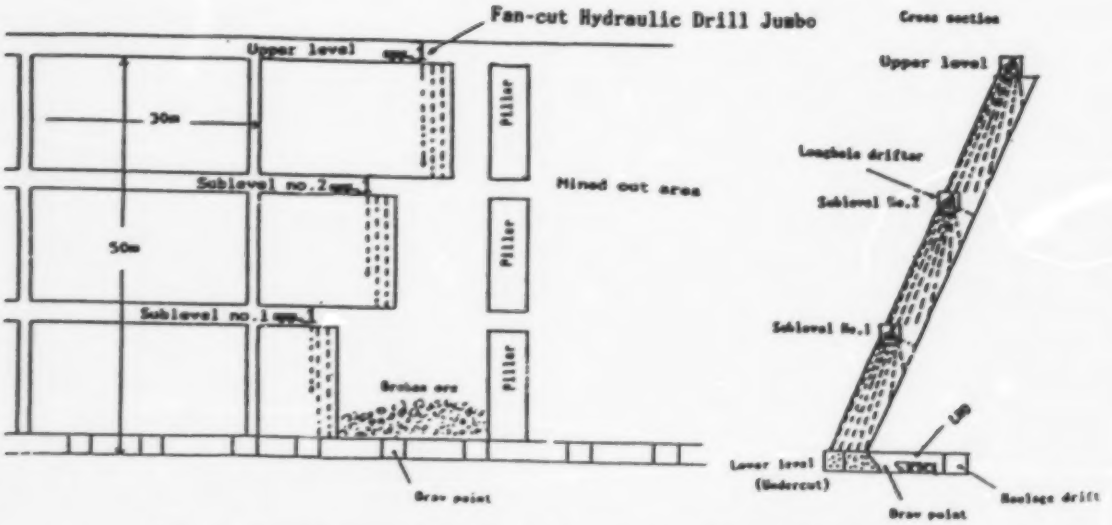


Fig. 2 General layout of sub-level stoping (by Fan-cut Drill)

At working faces where rock temperatures are higher than 70 degrees centigrade, heatproof electric caps and emulsion explosives are used.

Soon after sub-level stoping is finished, the stope is filled with the waste from developments or tailing sand.

Underground Transportation:

The ore above and below -300ML are transported to -300ML and -600ML main bin near the No.6 shaft respectively. The tandem system trains, consisting of 4 tons battery locomotives and 1.5 cubic meter Granby cars are utilized.

Loading, winding and dumping from the lower ore bins to the upper ore bin (+40ML) are practised automatically through the No.6 vertical shaft. Then, the ore is hauled to milling plant by conveyer belt.

The waste from developments in the lower levels is hoisted through the No5. or No3. vertical shaft into the waste bins. It is dumped into the finished stope area by tandem system trains and / or LHDs.

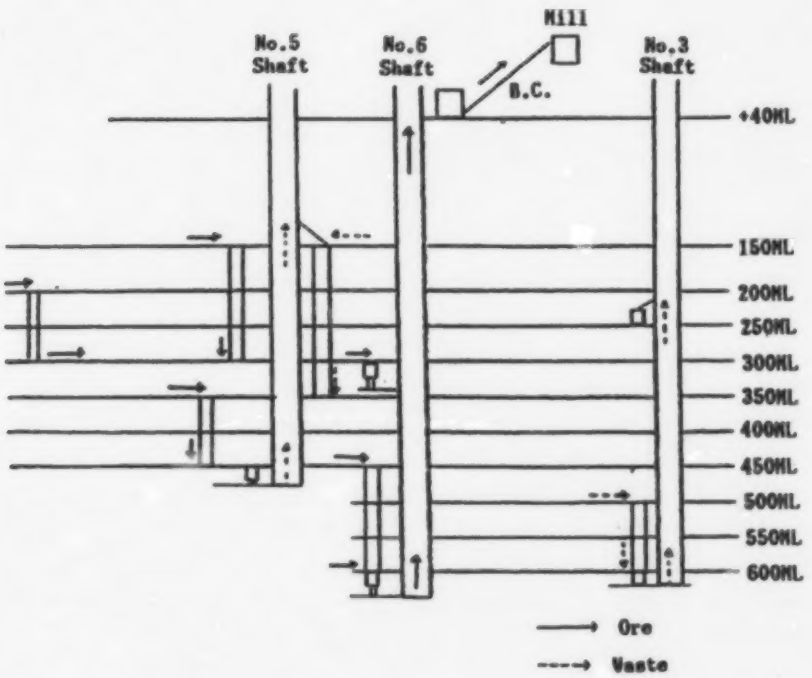


Fig. 3 Transportation system of Toyoha Mine.

Ventilation and Cooling:

As the working places move to northwesten or southeastern parts, or lower level, rock temperatures become higher. The deepest working faces are about 600m below surface. There, the virgin rock temperatures exceed 120 degrees centigrade. Under these conditions, the mechanical ventilation, the cooling by water, the drainage of hot ground water, the filling of the stopes, and the blocking off abandoned area are practised to lower the working face temperatures.

The ventilation system is diagonal, i.e., air enters through central shafts and exhausts through surrounding shafts.

Quantity of the intake airflow is about 20,000 cubic meters per minute (Fig.4).

Cooling is carried out in high temperature areas by water spray. The water is supplied from the Shirai river.

When the water temperature rises in summer, it is cooled by refrigerator. Besides water pipes are covered with heat insulating materials.

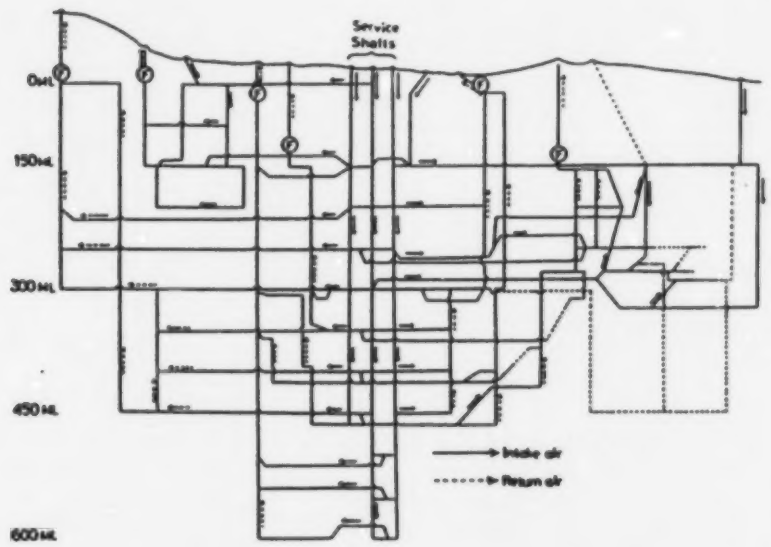


Fig. 4 Ventilation system of Toyoha Mine.

Drainage :

About 2 cubic meters per minute of ground water, and about 6 cubic meters per minute of service water for cooling and drilling from surface supply are pumped up from underground.

According to the difference of pH, it is divided into eastern and western systems, and drained to each settling pond.

The hot ground water is also pumped to the surface and utilized for baths and so on.

Development:

To develop a newly found ore deposit named Sinano, many development works are being carried out. These include a ramp from the surface, ventilation shafts and a main haulage tunnel at -600ML.

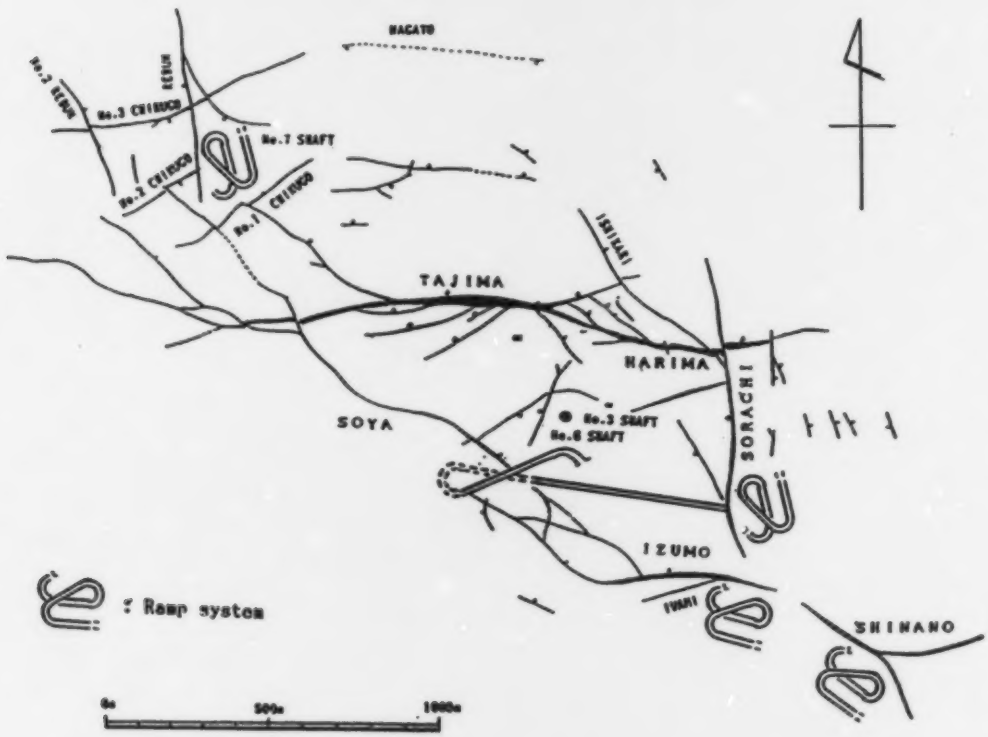


Fig. 5 Vein structure and Ramp systems of Toyoha Mine.

APPENDIX D. OUTLINE OF TOYOHA MILL[1]

[1] Toyoha Mines Co. Ltd. 1991.

1.GENERAL

The ore deposits of Toyoha mine are polymetallic veins. The principal economic minerals are sphalerite and silver minerals. The gangue minerals are mainly quartz, chlorite, calcite, and sericite.

The original milling started at Ishiyama 30 km away from the mine site in 1939 having the capacity of 10,000 tons per month. The current concentrator put in operation at the mine site in April 1969, now treats 45,000 tons per month, producing lead, zinc and pyrite concentrates. These concentrates are transported to Otaru port by trucks followed by shipment to domestic smelters. The concentrator operates 3 shifts per day of 8 hours, 5-6 days/week by 16 operators. The total man power is 38 persons. Consumption of electricity is the concentrator is 44 kwh/tons.

2.CRUSHING

The crushing section in the mill employs an open circuit system, producing -18 mm ores. The schimatic figure of the crushing circuit is shown in Figure 1.

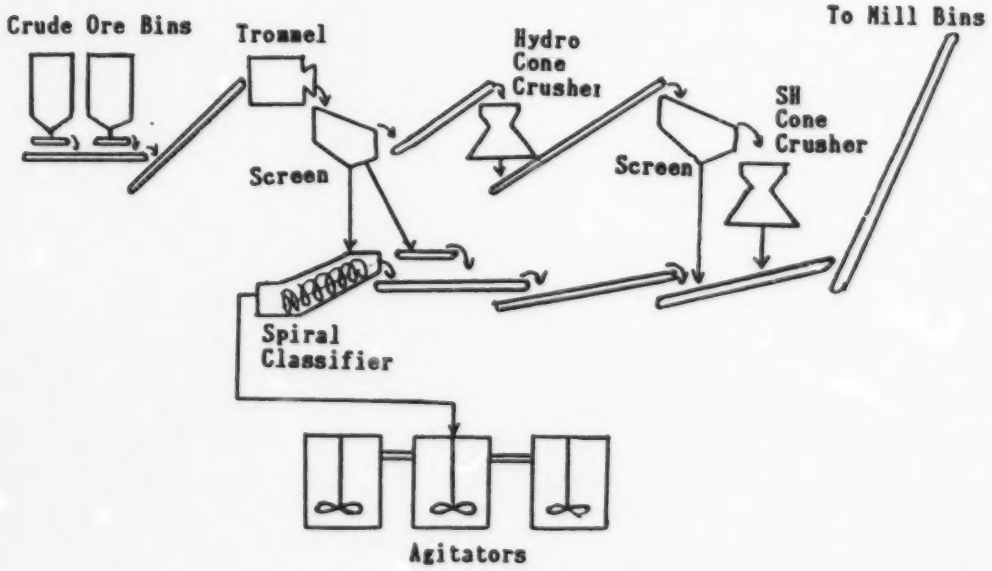


Figure 1. Crushing Circuit

Primary crushing is carried out underground. The hoisted ore is conveyed to two 400 tons crude ore bins. The ore drawn from the bins is washed by a 2.4 mϕ x 3.0 m drum scrubber with trommel prior to secondary crushing.

The undersize product of the trommel(-65 mm) is passed through a 1.5 m x 3.6 m double deck low head screen (primary screen). The oversize product of the trommel and the oversize of the upper deck of the screen (-65 mm +15 mm) are jointly fed to a 1260 mm ϕ hydrocone crusher (secondary crusher). The secondary crusher product is fed to a 1.8 m x 3.6 m single deck low head screen (secondary screen). The oversize product of the secondary screen (+18 mm) is fed to a 1,800 mm ϕ short head cone crusher (tertiary crusher) The tertiary crusher product and the undersize product of secondary screen are conveyed to seven 500 fine ore bins.

The undersize product of the lower deck of the primary screen is fed to a 1.65 m ϕ spiral classifier. The rake up sand of the classifier and oversize product of the lower deck of the primary screen are sent to the fine ore bins. The overflow of the classifier is pumped to three agitators.

The crushing section is operated in 2 shifts per day of 8 hours, treating 180 tons per hour.

3.GRINDING

Grinding is carried out by a conventional combination of a 3.0 m ϕ x 3.6 m rod mill and a 3.0 m ϕ x 4.8 m ball mill in closed circuit with a 2.1 m ϕ duplex spiral classifier, and two 500 mmϕ cyclones.

The slime from the agitators is fed to the duplex spiral classifier. The cyclone overflow at approximately 60 % minus 200 mesh is sent to the flotation circuit. The schimatic figure of the grinding circuit is shown in Figure 2.

The consumption of the rod and ball is each 420 and 450 g/t. The milling capacity of the grinding circuit is 100 tons per hour.

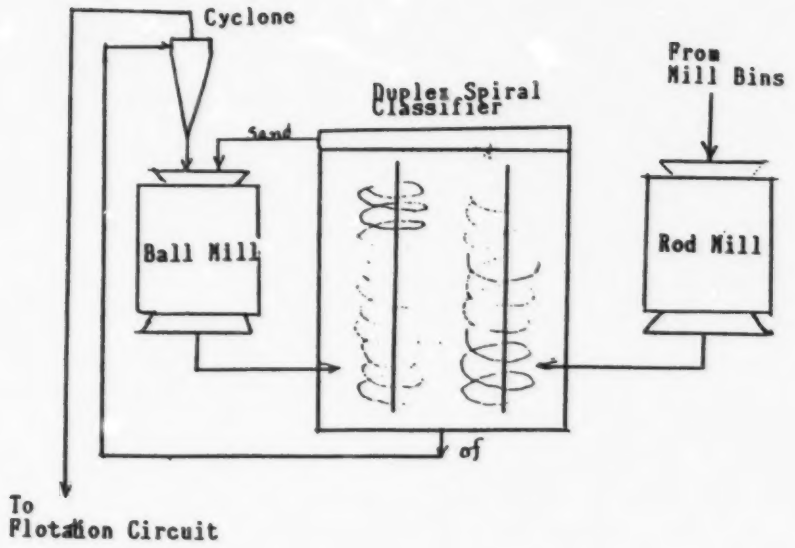


Figure 2. Grinding Curcuit

4.FLOTATION

Three different concentrates(lead, zinc, pryrite) are produced by straight selective flotation in the flotation section.

Rougher flotation equipment consists of No.48 Warman cells, while cleaner flotation equipment consists of No.24 FW cells. In October 1988, 8 column flotation cells and 46 No.48 Agitair cells were introduced aiming at 20 % increase of mill capacity and higher grade of lead and zinc concentrates. Saplified flowsheet of flotation is shown in Figure 3.

1)Lead flotation

Lead rougher flotation consists of a bank of 16 No.48 Warman cells and 6 Agitair cells and a bank of 18 No.48 Warman cell and 4 Agitair cells. Rougher concentrates after being reground, are fed to a 2.1 mϕ x 13.5 m H column flotation cell. The cleaner concentrates are recleaned by a 1.5 m ϕ x 9.5 m H column flotation cell. The recleaner tailings are returned to the cleaner cell. The cleaner tailing are scavenged in 8 No.24 FW cells.

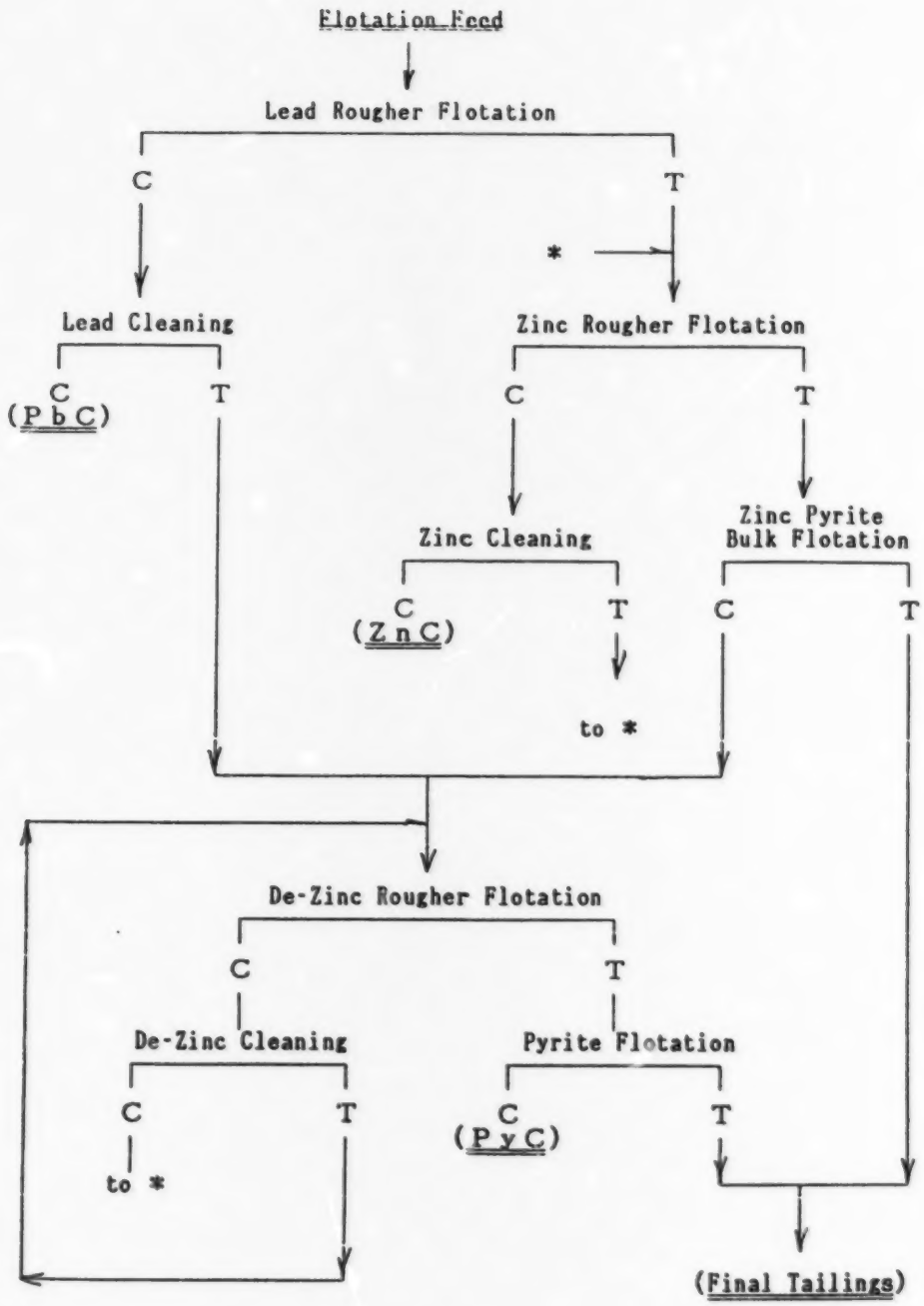


Figure 3. Simplified Flowsheet of Flotation

The lead circuit uses #404 aeropromoter and propyl xanthate as lead collectors with SO_2 and sodium cyanide to depress the zinc and iron. The rougher flotation is carried out at pH 6.3 - 7.0. In cleaner flotation circuit, sodium cyanide and activated carbon are used. Pine oil and Takasa froth are used as the frother.

2)Zinc flotation

Zinc rougher flotation is carried out in three banks of 16 No.48 Warman cells and 6 Agitair cells. Rougher concentrates after being reground are fed to a 2.7 m ¢ x 13.5 m H cleaner column. The cleaner tailings are scavenged by 12 No.24 FW cell.

Zinc flotation uses copper sulphate as a zinc activator and propyl xathate as colletors. The zinc rougher flotation is regurated at pH 8.5 with lime. The zinc cleaner flotation is conditioned with lime (pH 12) and activated carbon.

3)Zinc - pyrite bulk flotation

The zinc rougher tailing are reground, then zinc - pyrite bulk flotation carried out in 20 No.48 Warman cells and 22 No.48 Warman cells The concentrates are transferred to de - zinc flotation. The tailing is the final tailings.

4)De-zinc flotation

The lead cleaner scavenger tailings are fed to a 1.8 m ¢ x 13.5 m H column. The concentrates of the 1.8 m ¢ column are fed to 2.7 m ¢ zinc cleaner.

The zinc - pyrite bulk flotation concentrates are reground and sent to de - zinc flotation. De - zinc flotation is carried out in a 2.7 m¢ x 13.5 m H column. The concentrates of the de-zinc flotation are further cleaned in a 2.4 m¢ x 13.5 m H column. The cleaner concentrates are treated in 2.7 m¢ zinc cleaner column. The tailings of 2.7 m¢ de-zinc column and the tailing of 1.8 m¢ column are scavenged in 18

No.48 Agitair cells. De-zinc scavanger tailings are advanced to pyrite flotation.

5)Pyrite flotation

Pyrite flotation is carried out in 6 No.24 FW cells. The pyrite flotation tailings and zinc - pyrite bult flotation tailings are sent to a tailing dam.

5.THICKENING, FILTERING, AND SHIPMENT

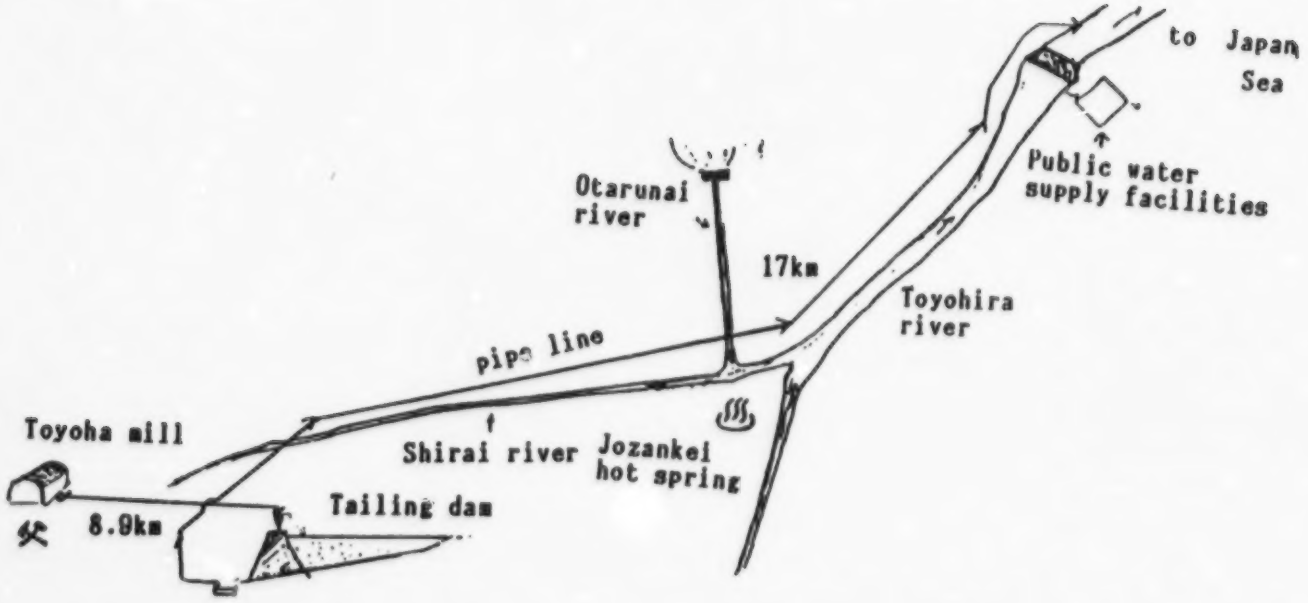
Each concentrate is thickened in the thickner, then transferred to a filtering plant 800 m away from the concentrator. Lead and pyrite concentrates are filtered by drum filters. Zinc concentrates are filtered by a PF32 LAROX pressure filter. The moisture content of the concentrates is 7 - 8 %. Lead and zinc concentrates are transferred by 11 tons trucks to Otaru port, followed by shipment to domestic smelters. Pyrite concentrates are trasferred to Tomakomai port, followed by shipment to oversea and domestic smelters.

6.TAILINGS DISPOSAL

Flotation tailings and mine water are mixed and regurated with lime (pH 10) to precipitate heavy metal ions (mainly manganese, zinc and iron), then pumped by two centrifugal pumps to the tailing dam situated 9 km away from the concentrator. The tailing dam is constructed to impound 5.7 million m^3 and the hight of the embankment is 100 m. The decanted water is regurated pH 7 - 8 with sulfuric acid. The regurated water is transferred 17 km away from the tailing dam to a farther discharge point of public water supply facilities located down the river.

7.WATER SUPPLY

Purified mine water is used for milling process. Overflow of each thickner are recycled. Additional water is obtained from the river.


to Japan Sea
Public water supply facilities
Otarunai river
17km
Toyohira river
pipe line
Toyoha mill
Shirai river
Jozankei hot spring
Tailing dam
8.9km

MILLING OPERATION OF TOYOHA MINE (Budget for the last half of 1991)

METALLURGICAL BALANCE

		ASSAYS (g/t %)					DISTRIBUTION (%)					
	(T/M)	Ag	Cu	Pb	Zn	S	Wt	Ag	Cu	Pb	Zn	S
Feed	46,000	213	0.33	1.52	9.62	18.00	100.0	100.0	100.0	100.0	100.0	100.0
Cu Conc.	314	3,050	22.00	6.00	4.00	35.00	0.7	9.8	45.5	2.7	0.3	1.1
Pb Conc.	777	4,400	1.50	67.00	4.50	18.00	1.7	34.9	7.7	74.5	0.8	1.4
Zn Conc.	7,400	480	0.55	1.20	57.40	32.00	16.1	36.3	26.8	12.7	96.0	23.4
Py Conc.	4,650	100	0.30	0.25	0.40	49.00	10.1	4.7	8.2	1.7	0.4	22.5
Tailings	32,859	44	0.05	0.18	0.34	15.90	71.4	14.3	10.8	8.4	2.5	51.6

MILL PERSONNEL

Staff	11
Crushing Operator	2
Grinding Operator	3
Flotation Operator	3
Filter Operator	4
Waste Treatment	2
Miscellaneous	1
Mechanics	5
Laboratory	1
Assayer	4
Clerk	1
TOTAL	37

POWER REQUIREMENTS

	MWH/M	kwh/t
Crushing	120	2.6
Grinding	500	10.9
Flotation	800	17.4
Filtering	145	3.2
Tailings	300	6.5
Misc.	205	4.5
TOTAL	2070	45.0

CONSUMPTION OF GRINDING MEDIA

	g/t
30 mm ¢ balls	235
50 mm ¢ balls	435
75 mm ¢ rods	530
TOTAL	1200

REAGENT CONSUMPTION (g/t FEED)

	Pine Oil	Takasa froth	NaPX	AP #404	AP #3501	Sulfer (SO2)	CuSO4	NaCN	Dex trin	Active Carbon	Lime
Pb Rougher flot.	32	4	5	30		60		9			
ZN Rougher flot.	8	6	45			40	300				pH 9.4
Zn, Py Bulk flot.			20		10		20				
Cu flot.						50			50	6	
Pb Cleaning flot.			3					12		25	
Zn Cleaning flot.			2				20			25	pH 11.5
DeZn Flotation		8	15				180	5		10	pH 10.2
Py Flotation			20								
TOTAL	40	18	110	30	10	150	500	26	50	66	